

AZ

PATENT SPECIFICATION

1.199,641



NO DRAWINGS

1.199,641

Inventors: GREGOIRE KALOPISSIS, ANDREE BUGAUT and HUBERT GASTON-BRETON

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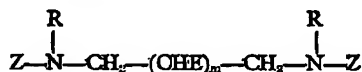
COMPLETE SPECIFICATION

New Anthraquinone and Nitro Dyestuffs

We, L'OREAL, a French Body Corporate of 14, rue Royale, Paris, France, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

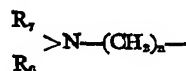
The present invention relates to novel dyestuffs.

More particularly, the present invention relates to compounds of the formula:

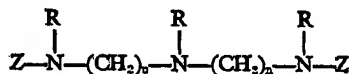


I

wherein each of the Z radicals, which may be the same or different, represents a nitrobenzene or anthraquinone radical, at least one of which 2 radicals being substituted by an amino radical, which is unsubstituted or substituted by one or two alkyl, hydroxyalkyl, amino alkyl, monoalkylaminoalkyl or dialkylaminoalkyl radicals, the alkyl radicals in the said substituents containing 1 to 4 carbon atoms, or by an alkyl or alkoxy radical containing 1 to 4 carbon atoms; E represents a hydrogen atom or a hydroxyl radical; m is 0, 1, 2, 3 or 4; and each of the R radicals, which may be the same or different, represents a hydrogen atom, an alkyl or hydroxyalkyl radical containing 1 to 4 carbon atoms or a radical of the formula:



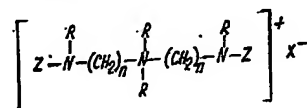
wherein n is 2, 3, 4, 5 or 6; and each of R₁ and R₂, which may be the same or different, represents a hydrogen atom or an alkyl radical containing 1 to 4 carbon atoms, subject to the proviso that at least one of R₁ and R₂ represents a said alkyl radical, or R₁ and R₂ together with the nitrogen atom to which they are attached form a heterocyclic ring, with the proviso that when E represents a hydroxyl radical m is not 2, and acid addition salts and quaternary ammonium salts thereof. It also relates to the similar compounds of the formulae:



(II)

[Price

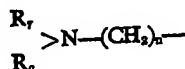
and acid addition salts and quaternary ammonium salts thereof, and



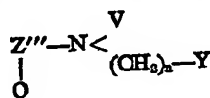
(II)

wherein R and each of the n values, which may be the same or different, are defined above, and X represents a halogen atom. In one embodiment, E represents a hydrogen atom, one of the R radicals does not represent an alkyl radical of 1 to 4 carbon atoms and at least one of the Z radicals represents a nitrophenyl radical which is substituted by an amino radical which is unsubstituted or substituted by one or two alkyl, hydroxyalkyl or aminoalkyl radicals of 1 to 4 carbon atoms, or an anthraquinone radical substituted by an amino radical which is unsubstituted or substituted by one or two alkyl radicals of 1 to 4 carbon atoms. In another embodiment, one of the Z radicals represents a nitrophenyl radical substituted by an alkoxy radical of 1 to 4 carbon atoms, and the other Z radical represents a nitrophenyl radical substituted by an amino radical which is unsubstituted or substituted by one or two alkyl, hydroxyalkyl or aminoalkyl radicals of 1 to 4 carbon atoms. In a further embodiment, at least one of the Z radicals represents a nitrophenyl radical substituted by an amino radical which is unsubstituted or substituted by one or two alkyl, hydroxyalkyl or aminoalkyl radicals of 1 to 4 carbon atoms.

The present invention also provides a process for preparing a compound of formula I, II or III as set out above, in which each of the Z radicals, which may be the same or different, represents a nitrobenzene or anthraquinone radical, at least one of which Z radicals being substituted by an amino radical, which is unsubstituted or substituted by one or two alkyl, hydroxyalkyl, amino alkyl, monoalkylaminoalkyl or dialkylaminoalkyl radicals, the alkyl radicals in the said substituents containing 1 to 4 carbon atoms, or by an alkyl or alkoxy containing 1 to 4 carbon atoms; E represents a hydrogen atom or a hydroxyl radical; m is 0, 1, 2, 3 or 4; and each of the R radicals, which may be the same or different, represents a hydrogen atom, an alkyl or hydroxyalkyl radical containing 1 to 4 carbon atoms or a radical of the formula:—

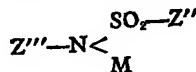


wherein n is 2, 3, 4, 5 or 6; and each of R₁ and R₂, which may be the same or different, represents a hydrogen atom or an alkyl radical containing 1 to 4 carbon atoms, subject to the proviso that at least one of R₁ and R₂ represents a said alkyl radical, or R₁ and R₂ together with the nitrogen atom to which they are attached form a heterocyclic ring, and X represents a halogen atom, which comprises condensing a compound of the formula (IV)



in which Y represents a halogen atom, an alkali metal or alkaline earth metal atom, or a primary, secondary or tertiary amine group, Q represents a hydrogen or halogen atom such as chlorine or bromine, V is the same as R, as hereinbefore defined, or represents the radical SO₂-Z'' in which Z'' represents a phenyl or tolyl radical, with

(i) a compound of the formula:



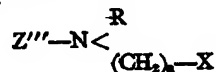
if Y represents a halogen atom;

(ii) a compound of the formula:



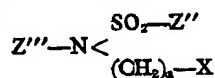
in which Q₁ represents a mobile group, such as a nitro group or halogen atom, which

is readily substituted by an amino group if Y represents a primary amino group;
 (iii) a compound of the formula:

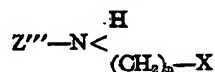


if Y represents a secondary or tertiary amino group;

(iv) a compound of the formula:



or of the formula:

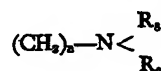


if Y represents an alkali metal or alkaline earth metal and n in formula IV is 0,
 and hydrolysing the SO_2-Z'' group;

and, optionally reacting the resulting compound so as to replace Q by a radical
 of the formula:



in which R_s represents hydrogen atom, an alkyl, hydroxyalkyl or alkoxyalkyl group,
 the alkyl groups of which substituents containing 1 to 4 carbon atoms, or a radical
 of the formula:

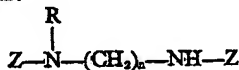


in which each of R_s and R_n , which may be the same or different, represents a hydrogen
 atom, or an alkyl or hydroxyalkyl radical of 1 to 4 carbon atoms or an acetyl radical
 or, together with the nitrogen atom to which they are attached, form a heterocyclic
 ring,

in which Z''' is the same as, or is a radical capable of being converted during
 the course of the reaction into Z and when Z''' is not the same as Z converting it
 thereto, X represents a halogen atom, M represents an alkali metal or an alkaline earth
 metal atom and n is an integer from 2 to 6, except where indicated otherwise, and,
 optionally, hydrolysing the product.

Other processes for preparing the compounds of the present invention are as
 follows:

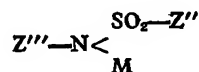
(1) A compound of the formula:



may be prepared by condensing a compound of the formula:

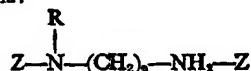


with a compound of the formula:

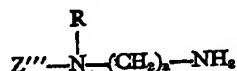


and hydrolysing the resulting product to remove the sulphonamide group.

(2) A compound of the formula:



may also be prepared by condensing a compound of the formula:

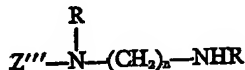


with a compound of the formula:



and, optionally, reacting the resulting compound with an amine.

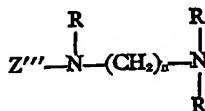
- 5 (3) A compound of formula II may be prepared by condensing a compound of the formula:



with a compound of the formula:



- 10 (4) A compound of formula III may be prepared by condensing, with quaternisation, a compound of the formula:

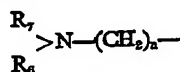


with a compound of the formula:

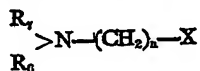


- 15 (5) A compound of formula I, II or III as defined in the main process in which least one of the R radicals represents a hydroxyalkyl radical may be prepared by reacting the corresponding compound in which at least one of the R radicals represents hydrogen with a hydroxyalkyl halide.

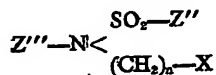
- 20 (6) A compound of formula I, II or III as defined in the main process in which at least one of the R radicals represents a radical of the formula:



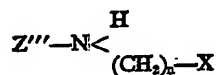
may be prepared by reacting the corresponding compound in which at least one of R radicals represents hydrogen with a halogenoalkylamine of formula:



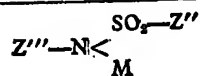
- 25 (7) A compound of formula I as defined in the main process may be prepared by condensing a compound of the formula:



or of the formula:

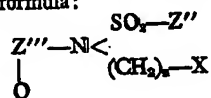


- 30 with a compound of the formula:

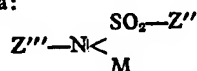


and hydrolysing the resulting product so as to remove the sulphonamide group or groups.

(8) A compound of formula I as defined in the main process may be prepared by condensing a compound of the formula:



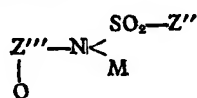
in which Q represents a halogen atom,
with a compound of the formula:



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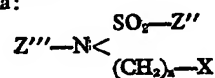
and reacting the resulting product with an amine of the formula: $\text{H}_2\text{N---R}_s$ and then hydrolysing to remove the sulphonamide groups.

(9) A compound of formula I as defined in the main process may be prepared by condensing a compound of the formula:

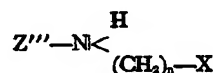


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in which Q represents a halogen atom,
with a compound of the formula:



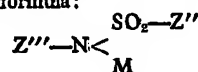
or of the formula:



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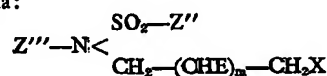
reacting the resulting product with an amine of the formula: $\text{H}_2\text{N---R}_s$ and then hydrolysing to remove the sulphonamide groups.

(10) A compound of formula I as defined in the main process may be prepared by condensing a compound of the formula:



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with a compound of the formula:



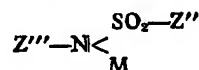
or of the formula:



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and hydrolysing the product to remove the sulphonamide group or groups.

(11) A compound of formula I as defined in the main process may be prepared by condensing a compound of the formula:



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with a dihalogenoalkane of the formula:

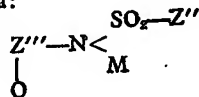


in the presence of dimethylformamide, and hydrolysing the sulphonamide groups.

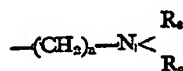
- 5 (12) A compound of formula I as defined in the main process may be prepared by condensing a dihalogenoalkane of the formula:



with a compound of the formula:



- 10 in which Q represents a halogen atom, such as chlorine or bromine, condensing the product with an amine of the formula: H_2N-R_5 in which R_5 represents an alkyl group of 1 to 4 carbon atoms, a hydroxyalkyl group of 1 to 4 carbon atoms, an alkoxyalkyl group or a radical of the formula:



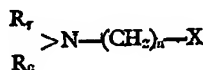
and hydrolysing the sulphonamide group.

- 15 The quaternary ammonium salts of compounds of formula I or II may be prepared by reacting a tertiary amino group present in a compound of formula I or II with an alkyl (of 1 to 4 carbon atoms) halide, an aryl halide or an alkyl (of 1 to 4 carbon atoms) sulphate.

- 20 The dyestuffs obtained may be modified in order to improve their water-solubility or to improve their affinity for certain fibres. Quaternisation is an illustration of this. This quaternisation does not produce any change of the fundamental colour of the compound where it is carried out on an extranuclear tertiary amino group i.e. a group which is not directly attached to an aromatic nucleus. By contrast, if it is carried out on a tertiary aromatic amino group, the fundamental colour may in certain cases change. Other conversions include introducing one or more hydroxyalkyl groups, for example by procedure (5) above, and introducing one or more aminoalkyl groups for example by reaction with a primary or secondary monohalogenoalkylamine of formula:



- 30 in which R_4 represents an alkyl radical of 1 to 4 carbon atoms; or with a tertiary amine of formula:



- 35 in which each of R_7 and R_6 , which may be the same or different, represents an alkyl radical of 1 to 4 carbon atoms; or R_7 and R_6 together with the nitrogen atom to which they are attached form a heterocyclic ring. In this latter case the aminoalkylation may, if desired, be followed by quaternisation.

It should be noted that these alkylations are generally accompanied by a deepening of the shade of the initial dyestuffs.

- 40 The compounds of the present invention may be used for a very large number of industrial applications. They may, for example, be used in the textile industry and, more particularly, in dyeing keratinic fibres, especially human hair.

- 45 It is known that the technique of dyeing different synthetic and natural fibres is based on the use of a varying number of individual dyestuffs used as a mixture. The behaviour of such mixtures during dyeing very frequently poses problems which are difficult to resolve, particularly as regards the harmonisation of the particular affinities of the dyestuffs and the harmonisation of the speeds at which the dyes are taken up by the fibres and of their fastness to washing. Users thus often find themselves in considerable difficulties both regarding the formulation of these mixtures and their application. The use of the dyestuffs of this invention partly

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resolves the problem since these dyestuffs have, in effect, the dyeing properties of the two dyestuffs from which they are derived.

5 Furthermore the dyestuffs of this invention have a considerable advantage over the so-called "disperse" dyestuffs which have hitherto been used for dyeing hair. Attempts have always been made, for dyeing hair, to use, as a balancing dyestuff, together with the direct dyestuffs, derivatives of nitro-para-phenylene diamine, dyestuffs normally used for dyeing wool ("disperse" dyestuffs). However the results always have something to be desired because these dyestuffs generally lack affinity for keratinic fibres (under the conditions under which hair is dyed) and because they have poor fastness to washing. 10

We have found that the dyestuffs of this invention, when used in the place of disperse dyestuffs, have better fastness to washing, and better affinity for the fibres.

15 The same advantages of improved fastness to washing and of affinity are found again when the products of this invention are compared with the use of disperse dyestuffs in the presence of solvents such as butyl glycol and benzyl alcohol, which is usually the procedure adopted for hair dyeing. 15

The dyestuffs of this invention furthermore have various other advantages which are in keeping with their relatively high molecular weight:

20 For example, it is often difficult to dye hair when part of its length has been moderately bleached. If one attempts to dye this hair one is, in effect, dealing with two types of fibres and this has always posed a difficult problem from the point of view of the affinity of the dyestuff for these two parts; this is the problem of selectivity. The use of the dyestuffs of the present invention enables a much more even dyeing to be obtained. This property may be connected with the relatively high molecular weights of these compounds and with the consequent reduction in penetration over the bleached part, since this is the part which takes dye more readily although we are not, of course, bound by this theory. 25

A parallel case may arise with hair which has previously been subjected to a permanent waving. In this case also one is dealing, during dyeing, with two parts, one part which has been permanently waved and the other (the root) being natural. The first part is easier to dye than the second so that a non-uniform dyeing may result. The dyestuffs of the present invention again enable a more uniform dyeing of such hair to be obtained. 30

It also been found that these dyestuffs are very suitable for dyeing strongly bleached hair, a case quite frequently found in practice, and that they give very valuable results. 35

Since these dyestuffs are polyfunctional they also afford extensive possibilities for all sorts of crosslinking and condensation reactions, and they can, for this reason, constitute valuable synthetic intermediates.

40 Thus the present invention also provides is a dyeing composition, in particular for keratinic fibres, especially human hair, which comprises at least one compound of the present invention in aqueous solution. It also provides a method of dyeing hair which comprises applying thereto a dyeing composition according to this invention, such as defined above, for 5 to 30 minutes at a temperature of 15° to 35°C, and then rinsing and dyeing the hair, optionally after washing it. 45

50 The dyeing compositions of this invention may contain any of the ingredients conventionally used in hair dyeing compositions such as organic solvents, perfumes, thickener, detergents (surface-active agents) and lacquers. The concentration of the dyestuffs in these compositions is preferably from 0.1% to 3%, for example from 0.2% to 3%, by weight. If desired any water-soluble dyestuffs according to the invention can be mixed with any other water-soluble dyestuff according to the invention or any known dyestuff which is suitable for dyeing keratinic fibres may be added, such as nitro-dyes, azo dyes and anthraquinone dyes. 50

The compositions preferably have a pH from 4 to 10, especially from 6 to 9.

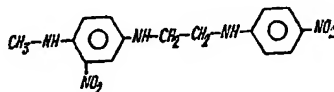
55 The following Examples further illustrate the present invention. 55

EXAMPLES OF PREPARATION

EXAMPLE 1

Preparation of N-[(3-nitro-4-methylamino)phenyl], N'-[(4'-nitro)phenyl]-ethylenediamine

of formula:



This product is obtained by condensing 4-nitro 1-N-benzene-sulphonyl, N-β-bromethylamino-benzene (a product subsequently referred to as A₁) with the potassium derivative of 1-N-methylamino-2-nitro-4-N'-benzene-sulphonylamino-benzene (a product subsequently referred to as B₁).

(A₁) is obtained by reacting 1,2-dibromethane with the potassium derivative of para-nitro-N-benzenesulphonylaniline in dimethylformamide in accordance with the process described in British Specification No. 1,164,824. This product is in the form of colourless crystals which, after recrystallisation from acetic acid, melt at 165°C.

The potassium derivative (B₁) has been described in British Specification No. 1,164,824.

1st stage: condensation

In order to condense (A₁) with (B₁) a mixture of 10 g (i.e. 0.026 mol) of compound (A₁) and 9 g (i.e. 0.026 mol) of compound (B₁) in 50 cm³ of dimethylformamide is heated at 120°C for 2 hours. After cooling the reaction mixture is poured onto a mixture of ice and water and the crude precipitated product is filtered off.

The crude product so obtained is purified by washing it with half-normal potassium hydroxide solution followed by washing with boiling water. In this way 14.3 g of N,N'-dibenzene-sulphonyl - N - [(3 - nitro - 4 - methylamino)phenyl] - N' - [(4' - nitro)phenyl]ethylenediamine, which, after recrystallisation from toluene, melts at 177°C, are obtained.

Analysis of the product obtained gives the following results:

Analysis	Calculated for C ₂₇ H ₂₈ N ₆ O ₈ S ₂	Found
N %	11.45	11.31 — 11.26
S %	10.47	10.60 — 10.45

2nd stage: hydrolysis

3 g (i.e. 0.0049 mol) of dibenzene-sulphonamide are dissolved in 18 cm³ of concentrated sulphuric acid and allowed to stand for 24 hours at ambient temperature. The mixture is then poured onto ice. The sulphate of the desired product is thus obtained, and it suffices to treat this with an aqueous sodium hydroxide solution to obtain N - [(3 - nitro - 4 - methylamino)phenyl], N' - [(4' - nitro)phenyl]-ethylenediamine.

This product is purified by recrystallisation from chlorobenzene. The crystals obtained are a violine (reddish violet) chestnut colour and melt at 185.5°C.

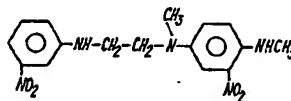
Analysis of the product obtained gives the following results:

Analysis	Calculated for C ₁₅ H ₁₇ N ₄ O ₄	Found
C %	54.38	54.47 — 54.44
H %	5.13	5.35 — 5.17
N %	21.14	21.17 — 21.04

EXAMPLE II

Preparation of N-[(3-nitro)phenyl], N'-methyl,N'-[(3'-nitro-4'-methylamino)-phenyl]ethylenediamine,

of formula:



This dyestuff is obtained in accordance with the process used for the preparation of the dyestuff of Example I, by condensing 1-N-methylamino-2-nitro-4-N'-methyl, N'-β-chlorethylamino-benzene (a product referred to below as A₂) with the sodium derivative of 3-nitro-1-N-benzenesulphonylamino-benzene (a product referred to below as B₂).

Compound (A₂) is described in British Specification No. 1,164,824.

Compound (B₂) was prepared from 3-nitro-1-benzenesulphonylamino-benzene (whose melting point is 134°C) by sodium substitution in sodium ethylate.

1st stage: condensation

The condensation is carried out as in Example I by heating equimolecular amounts of (A₂) and (B₂) in excess dimethylformamide at 120°C.

2nd stage: hydrolysis

The crude product so obtained is thereafter hydrolysed with concentrated sulphuric acid as in Example I and the desired base is liberated from its sulphate by reaction with an aqueous sodium hydroxide solution.

The product so obtained melts at 142.5°C after recrystallisation from chlorobenzene.

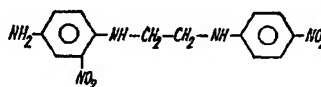
Analysis of the product obtained gives the following results:

Analysis	Calculated for C ₁₈ H ₁₉ N ₃ O ₄	Found
C %	55.65	55.46 — 55.53
H %	5.51	5.29 — 5.48
N %	20.28	20.50 — 20.30

EXAMPLE III

Preparation of N-[(2-nitro-4-amino)phenyl], N'-[(4'-nitro)phenyl]-ethylenediamine,

of formula:



This dyestuff is obtained by condensing 4-nitro-1-N-benzenesulphonyl, N-β-bromo-methylamino-benzene (A₁) with the sodium derivative of 1-N-benzenesulphonylamino-2-nitro-4-acetamino-benzene (a product referred to below as B₃), followed by a first hydrolysis with concentrated sulphuric acid in the cold in order to remove the benzenesulphonyl groups and a second hydrolysis with dilute hydrochloric acid in order to remove the acetyl group.

The preparation of the compound (A₁) has been mentioned in example I. The compound (B₃) is obtained in accordance with the process described in British Specification No. 1,164,824.

1st stage: condensation

A mixture of 33.8 g (i.e. 0.087 mol) of (A₁) and 31.2 g (i.e. 0.087 mol) of (B₂) in 150 cm³ of dimethylformamide is heated at 120°C for 2 hours. After cooling, the mixture is poured onto a mixture of water and ice and the crude product formed is then isolated.

This product is purified by treatment with a half-normal sodium hydroxide solution followed by washing with boiling water in order to remove a little of the initial 1-N-benzenesulphonylamino-2-nitro-4-acetaminobenzene. The amount of (A₁) which has not reacted is thereafter removed by successive hot extractions with cyclohexane.

In this way 36.6 g of N,N'-dibenzenesulphonyl, N-[(2-nitro-4-acetamino)phenyl], N'-[(4-nitro)phenyl]ethylenediamine are obtained in the form of a thick oil.

2nd stage: hydrolysis

3 g of this compound are dissolved in 15 cm³ of concentrated sulphuric acid and left in contact for 24 hours at ordinary temperature. The mixture is then poured onto ice and the precipitated product is filtered off.

In this way 1.2 g of N-[(2-nitro-4-acetamino)]phenyl, N'-[(4'-nitro)phenyl]-ethylenediamine melting at 247°C are obtained.

The hydrolysis is thereafter continued by heating under reflux with concentrated hydrochloric acid (20 cm³); after cooling the reaction mixture, the product in the form of the hydrochloride is filtered off. The base is liberated by treating this with an aqueous sodium hydroxide solution. 0.7 g of N-[(2-nitro-4-amino)phenyl], N'-[(4'-nitro)phenyl]ethylenediamine are filtered off; after recrystallisation from chlorobenzene this material melts at 177°C and is in the form of deep chestnut-coloured crystals.

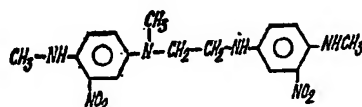
Analysis of the product obtained gives the following results:

Analysis	Calculated for (C ₁₄ H ₁₅ N ₅ O ₄)	Found
C %	53.00	53.25 — 53.03
H %	4.72	4.82 — 4.80
N %	22.08	21.90 — 21.88

EXAMPLE IV

Preparation of N-methyl, N-[(3-nitro-4-methylamino)]phenyl, N'-[(3'-nitro-4'-methylamino)phenyl]ethylenediamine,

of formula:



This dyestuff is obtained by condensing 1-N-methylamino-2-nitro-4-N'-methyl, N'-β-chlorethylamino-benzene (a product subsequently referred to as A₄) with the potassium derivative of 1-N-methylamino-2-nitro-4-N'-benzenesulphonylamino-benzene (a product subsequently referred to as B₄), followed by hydrolysing with sulphuric acid.

The compounds (A₄) and (B₄) are described in British Specification No. 1,164,824.

1st stage: condensation

A mixture of 24.4 g (i.e. 0.1 mol) of (A₄) and 34.5 g (i.e. 0.1 mol) of (B₄) in 100 cc of dimethylformamide is heated for 2 hours on a boiling water bath.

After cooling, the mixture is poured onto a solution of 2-normal ice-cold hydrochloric acid solution and the crude product is filtered off in the form of the hydrochloride. This hydrochloride is treated with a 2-normal sodium hydroxide solution and 30 g of N-[(3-nitro-4-methylamino)phenyl], N-methyl, N'-benzenesulphonyl, N'-[(3'-

nitro-4'-methylamino)phenyl]ethylenediamine, which after recrystallisation from methyl isobutyl ketone melts at 140°C, are filtered off.

Analysis of the product obtained gives the following results:

Analysis	Calculated for $C_{22}H_{20}O_2N_4S$	Found
N %	16.34	16.27 — 16.40
S %	6.22	6.18 — 6.40

2nd stage: hydrolysis

20 g of this product are dissolved in 100 cc of concentrated sulphuric acid. The reaction mixture is left at ambient temperature for 24 hours and then poured onto ice. The mixture is rendered alkaline and 13 g of N-[(3-nitro-4-methylamino)phenyl], N-methyl, N'-[(3'-nitro-4'-methylamino)phenyl]ethylenediamine, which after recrystallisation from toluene melts at 167°C, are filtered off.

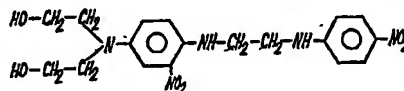
Analysis of the product obtained gives the following results:

Analysis	Calculated for $C_{17}H_{15}N_3O_4$	Found
C %	54.54	54.69 — 54.68
H %	5.88	5.88 — 5.90
N %	22.46	22.40 — 22.22

EXAMPLE V

Preparation of N-[(2-nitro-4-di-β-hydroxyethylamino)phenyl], N'-[(4'-nitro)phenyl]ethylenediamine,

of formula:



6.3 g (i.e. 0.02 mol) of N-[(2-nitro-4-amino)phenyl], N'-[(4'-nitro)phenyl]-ethylenediamine are heated under reflux with a solution of 14.3 g of 70% pure glycol bromhydrin (i.e. 0.08 mol) in the presence of 4 g of calcium carbonate on a boiling water bath for 2 hours 30 minutes. At the end of the reaction, the reaction mixture is poured onto a mixture of 150 g of water and ice. The crude product precipitated in this way is filtered off and then dissolved hot in 3-normal hydrochloric acid (about 100 cm³); on cooling, the hydrochloride of the desired product crystallises out.

After filtering, the desired base is recovered by rendering alkaline with dilute ammonia. The precipitated base is filtered off, dried, and then recrystallized from a mixture of chloroform and alcohol.

The product is in the form of brown crystals which melt at 148°C.

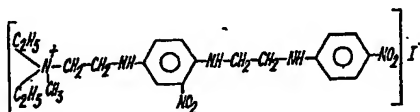
Analysis of the product obtained gives the following results:

Analysis	Calculated for $C_{18}H_{23}N_5O_6$	Found
C %	53.33	55.50 — 53.48
H %	5.68	5.80 — 5.52
N %	17.29	17.22 — 17.11

EXAMPLE VI

Preparation of N-[(2-nitro-4- β -diethylmethyllumonium-ethylamino)phenyl],
N'-[(4'-nitro)phenyl]ethylenediamine iodide,

of formula:



1st stage: preparation of N-[(2-nitro-4-benzenesulphonylamino)phenyl], N'-[(4'-nitro)phenyl]ethylenediamine.

0.022 mol of benzenesulphonyl chloride are added to a solution of 0.02 mol of N-[(2-nitro-4-amino)phenyl], N'-[(4'-nitro)phenyl]ethylenediamine (i.e. 6.3 g) in 60 cm³ of pyridine, and the reaction mixture is then kept at 45°C for 1 hour. It is then poured onto 60 cm³ of concentrated hydrochloric acid to which 200 g of crushed ice has been added and 8.3 g of a crude product are filtered which, after recrystallisation from pyridine diluted with an equal volume of water, melts at 130°C.

Analysis of the product obtained gives the following results:

Analysis	Calculated for $C_{20}H_{19}N_5O_6S$	Found
N %	15.32	15.55 — 15.51
S %	7.00	6.92 — 7.05

2nd stage: preparation of N-[(2-nitro-4-(benzenesulphonyl- β -diethylaminoethyl)-amino)phenyl], N'-[(4'-nitro)phenyl]ethylenediamine.

0.15 mol of the benzenesulphonamide previously obtained in the first stage (i.e. 7 g) are added to 70 cm³ of a normal sodium hydroxide solution at 80°C in such a way as to dissolve the material completely. After cooling, 7.1 g of the sodium derivative are filtered off.

This sodium derivative is dissolved in 70 cm³ of dimethylformamide at 90°C and 0.03 mol of diethylaminoethyl chloride are added quite rapidly. After having kept the reaction mixture at 90°C for 10 minutes, it is poured on to 100 cm³ of iced water and the crude product is filtered off. The crude product is treated with 200 cm³ of 0.25-normal sodium hydroxide solution in order to remove unreacted starting product, and is washed with water and dried. 6 g of N-[(2-nitro-4-(benzenesulphonyl- β -diethylaminoethyl)amino)phenyl], N'-[(4'-nitro)phenyl]ethylenediamine are obtained.

3rd stage: preparation of N-[(2-nitro-4- β -diethylaminoethylamino)phenyl], N'-[(4'-nitro)phenyl]ethylenediamine.

0.01 mol of the previously obtained disubstituted benzenesulphonamide (i.e. 5.6 g) are dissolved in 28 cm³ of concentrated sulphuric acid and the solution is left for 3 hours at ambient temperature.

The reaction mixture is poured onto 300 cm³ of ice, rendered alkaline, and the N - [(2-nitro-4-β-diethylaminoethylamino)phenyl], N' - [(4'-nitro)phenyl]ethylenediamine is extracted by means of methyl isobutyl ketone.

The solvent is driven off, and the residue is dissolved in 100 cm³ of a 2-normal hydrochloric acid solution on a boiling water bath.

After cooling, 3.5 g of the expected product are filtered off in the form of the dihydrochloride which after recrystallisation from 2-normal hydrochloric acid melts at 125°C with decomposition.

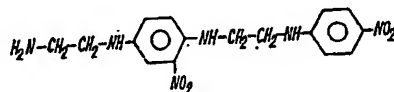
4th stage: preparation of [(2-nitro-4-β-diethylmethylammoniumethylamino)phenyl], N' - [(4'-nitro)phenyl]ethylenediamine.

0.1 mol of N - [(2-nitro-4-β-diethylaminoethylamino)phenyl], N' - [(4'-nitro)phenyl]ethylenediamine (i.e. 4.2 g) are dissolved in 60 cm³ of chlorobenzene. 1.5 g of methyl iodide are added; the reaction mixture is left for five hours at ambient temperature and the quaternary compound is filtered off.

EXAMPLE VII

Preparation of N - [(2-nitro-4-β-aminoethylamino)phenyl], N' - [(4'-nitro)phenyl]ethylenediamine,

of formula:



A mixture of 0.024 mol of N - [(2-nitro-4-amino)phenyl], N' - [(4'-nitro)phenyl]ethylenediamine (i.e. 7.65 g) and 0.028 mol of β-bromomethylamine hydrobromide (i.e. 5.75 g) in 150 cm³ of propanol and 15 cm³ of water is heated in the presence of 1.4 g of calcium carbonate for 7 hours on a boiling water bath. The boiling reaction mixture is filtered off, the filtrate is cooled and 6.6 g of a crude product in the form of the monohydrobromide are filtered off. This material is redissolved in boiling water, filtered hot and rendered alkaline with a sodium hydroxide solution. After cooling, 5.8 g of N - [(2-nitro-4-β-aminoethylamino)phenyl], N' - [(4'-nitro)phenyl]ethylenediamine are filtered off.

This product is dissolved in hot 2-normal hydrochloric acid. After cooling, the expected product is filtered off in the form of the dihydrochloride. It melts at 150°C with decomposition.

Analysis of the product obtained gives the following results:

Analysis	Calculated for C ₁₆ H ₂₂ N ₆ O ₄ Cl ₂ ·H ₂ O	Found
C %	42.57	43.14 — 43.06
H %	4.92	5.02 — 5.07
N %	19.06	18.75 — 18.56

EXAMPLE VIII

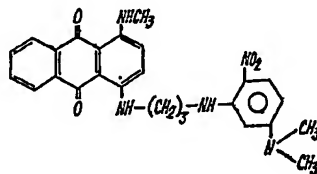
Preparation of N - [(3-nitro-4-methylamino)phenyl], N-β-[(3'-nitro-4'-methylamino)phenyl]aminoethyl, N,N-dimethylammonium iodide.

5 g of N-methyl, N - [(3-nitro-4-methylamino)phenyl], N' - [(3'-nitro-4'-methylamino)phenyl]ethylenediamine are dissolved in 50 cm³ of chlorobenzene. 2 g of methyl iodide are added and the reaction mixture is kept at 50°C for 10 hours. The quaternary compound formed is thereafter isolated.

EXAMPLE IX

Preparation of 1-methylamino-4-γ-[(2'-nitro-5'-dimethylamino)phenyl]amino-propylaminoanthraquinone,

of formula:



This product is obtained by condensing 1-methylamino-4-γ-aminopropylaminoanthraquinone (a product hereafter referred to as A₉) with 3,4-dinitro-N,N-dimethylaniline (a product hereafter referred to as B₉).

Condensation of A+B

3.1 g (i.e. 0.01 mol) of 1-methylamino-4-γ-aminopropylaminoanthraquinone and 1.1 g (i.e. 0.005 mol) of 3,4-dinitro-N,N-dimethylaniline in 40 cm³ of xylene are heated under reflux for half an hour. After cooling, 20 cm³ of hexane are added and 2.9 g of crude product are filtered off.

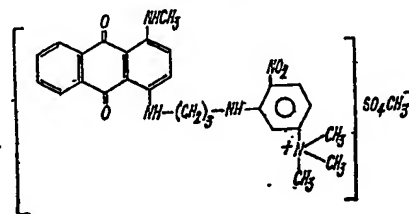
Chromatographic study of this product shows the presence of small amounts of the initial anthraquinone derivative and of traces of a dinitrated derivative.

In order to remove the anthraquinone derivative used as the starting material, the crude product is washed with a normal solution of hydrochloric acid. Thereafter the traces of the dinitrated derivative are removed by converting it to 1-N,N-dimethylamino-3-β-aminoethylamino-4-nitrobenzene by heating the crude product with an excess of ethylenediamine. After having driven off the excess ethylenediamine in vacuo, the product is washed with water and then with a normal hydrochloric acid solution until the wash waters are no longer yellow. In this way 1.6 g of the expected product, which melts at 227°C, are obtained.

EXAMPLE X

Preparation of [1-methylamino-4-γ-[(2'-nitro-5'-trimethylammonium)phenyl]-aminopropylaminoanthraquinone] methylsulphate,

of formula:



1.6 g of 1-methylamino-4-γ-[(2'-nitro-5'-dimethylamino)phenyl]aminopropylaminoanthraquinone, this product having been obtained previously, are dissolved in chlorobenzene under reflux. An excess of methyl sulphate is added and the mixture heated under reflux for half an hour. After cooling, 2 g of [1-methylamino-4-γ-[(2'-nitro-5'-trimethylammonium)phenyl]aminopropylaminoanthraquinone] methylsulphate are filtered off.

This product is obtained by condensing 1-N,N-dimethylamino-3-dimethylamino-propylamino-4-nitrobenzene (a product hereafter referred to as A₁₁) with 4-nitro-1-β-bromomethylaminobenzene (a product hereafter referred to as B₁₁).

The product (A₁₁) is described in British Specification No. 1,127,080.

The compound (B₁₁) is obtained by hydrolysis of 4-nitro-1-N-benzenesulphonyl, N-β-bromomethylaminobenzene in concentrated sulphuric acid.

A mixture of 1.4 g (i.e. 0.005 mol) of (A₁₁) and 1.2 g (i.e. 0.005 mol) of compound (B₁₁) in 10 cm³ of chlorobenzene is heated for half an hour under reflux.

On cooling the reaction mixture the quaternary compound, which is initially oily, crystallises. After recrystallisation from boiling water it melts at 150°C with decomposition.

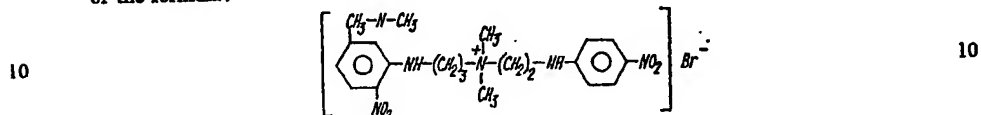
Analysis of the product obtained gives the following results:

Analysis	Calculated for $C_{21}H_{31}N_4O_4Br$	Found
C %	49.31	49.12 — 49.20
H %	6.06	6.26 — 6.29
N %	16.43	16.25 — 16.39

EXAMPLE XI

Preparation of [γ -N-[(2-nitro-5-dimethylamino-phenyl)- β -aminopropyl-N'-(para-nitrophenyl)aminoethyl] dimethylammonium bromide

of the formula:



This product is obtained by the condensation of 1-N,N-dimethylamino-3-dimethylaminopropylamino-4-nitro-benzene (a product subsequently referred to as A₁₁) with 4-nitro-1- β -bromoethylamino-benzene (a product subsequently referred to as B₁₁).

15 Product (A)₁₁ is described in British Specification No. 1,127,080. Product (B)₁₁ is obtained by the hydrolysis of 4-nitro-1-N-benzenesulphonyl-N- β -bromoethylamino-benzene with concentrated sulphuric acid.

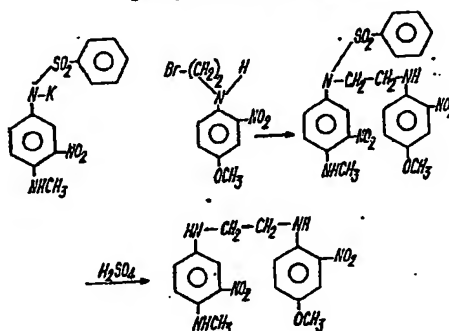
20 A mixture of 1.4 g. (0.005 mole) of (A₁₁) and 1.2 g. (0.005 mole) of B₁₁ is heated under reflux for $\frac{1}{2}$ hour with 10 cc. of chlorobenzene. After cooling the reaction mixture the quaternary salt, now oily, crystallises out. After recrystallisation from boiling water, it melts at 150°C. with decomposition.

The analysis of the product is as follows:

Analysis	Calculated for $C_{21}H_{31}N_4O_4Br$	Found
C %	49.31	49.12 — 49.20
H %	6.06	6.26 — 6.29
N %	16.43	16.25 — 16.39

EXAMPLE XII

Preparation of N-[(3-nitro-4-methylamino)phenyl]-N'-[(2'-nitro-4'-methoxy)-phenyl]ethylenediamine



5 First stage: preparation of N-benzenesulphonyl, N-[(3-nitro-4-methylamino)phenyl], N'-[(2'-nitro-4'-methoxy)phenyl]ethylenediamine. 5 *

0.61 mol of the potassium derivative of 1-N-methylamino-2-nitro-4-N'-benzenesulphonylamino benzene (i.e. 210 g) are dissolved in 850 cm³ of dimethylformamide which has been heated to 90°C beforehand. 0.16 mol (i.e. 167 g) of 1-methoxy-3-nitro-4-bromomethylaminobenzene prepared according to the process described in 10 British Specification No. 1,164,824 are added a little at a time with stirring. The reaction mixture is kept at 90°C for 20 minutes and is then cooled and poured into 3 litres of water. 300 g of N-benzenesulphonyl-N-[(3-nitro-4-methylamino)-phenyl], N'-[(2'-nitro-4'-methoxy)phenyl]ethylenediamine are filtered off which are 15 practically pure and which after recrystallisation from a mixture of dioxane and alcohol and drying in vacuo at 80°C melt at 115°C. 15

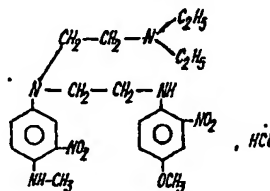
Second stage: preparation of N-[(3-nitro-4-methylamino)phenyl], N'-[(2'-nitro-4'-methylamino)phenyl], N'-[(2'-nitro-4'-methoxy)phenyl]ethylenediamine

0.59 mol of N-benzenesulphonyl, N-[(3-nitro-4-methylamino)phenyl], N'-[(2'-nitro-4'-methoxy)phenyl]ethylenediamine (i.e. 300 g) are added a little at a time, with 20 stirring, to 1200 cm³ of sulphuric acid whilst keeping the temperature at between 15 and 20°C. The reaction mixture is left at this temperature for 24 hours and then poured onto 5 kg of crushed ice, and the expected product is filtered off in the form of a sulphate. This sulphate is treated with 600 cm³ of pyridine at 60°C, with stirring. 25 The mixture is cooled, filtered, and 193 g of N-[(3-nitro-4-methylamino)phenyl], N'-[(2'-nitro-4'-methoxy)phenyl]ethylenediamine are washed with water; after recrystallisation from chlorobenzene this material melts at 152°C. 25

Analysis	Calculated for C ₁₈ H ₁₉ N ₅ O ₅	Found
C %	53.18	53.40 — 53.42
H %	5.26	5.35 — 5.46
N %	19.39	19.55 — 19.51

EXAMPLE XIII

Preparation of the monohydrochloride of N-β-diethylaminoethyl,N'-[(3-nitro-4-methylamino)phenyl],N'-[(2'-nitro-4-methoxy)phenyl] ethylenediamine

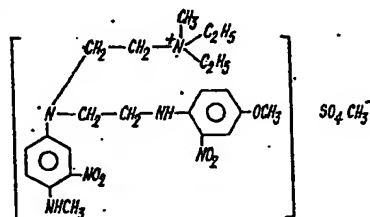


0.22 mol of N-[(3-nitro-4-methylamino)phenyl],N'-[(2'-nitro-4'-methoxy)-phenyl]ethylenediamine (i.e. 79.5 g) are dissolved in 600 cm³ of chlorobenzene under reflux. 1.1 mol of diethylaminoethyl chloride (i.e. 149 g) are added a little at a time with stirring and refluxing is continued for 4 hours. The mixture is cooled, 300 cm³ of petroleum ether are added and the expected monohydrochloride is filtered off in an impure state. After recrystallising the crude product from chlorobenzene, 96 g of N-β-diethylaminoethyl,N'-[3-nitro-4-methylamino)phenyl],N'-[2'-nitro-4'-methoxy)phenyl]ethylenediamine monohydrochloride are obtained in a pure state. This product melts at 158°C.

Analysis	Calculated for C ₂₃ H ₃₃ N ₃ O ₂ Cl	Found
C %	53.17	52.98 — 53.00
H %	6.65	6.55 — 6.62
Cl %	7.15	7.05 — 7.14

EXAMPLE XIV

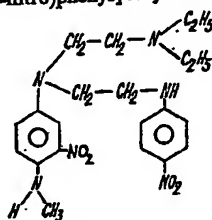
Preparation of β-[N-[(3-nitro-4-methylamino)phenyl],N-β'-N'-[(2'-nitro-4'-methoxy)phenyl]aminoethyl]aminoethyl methyl diethylammonium methylsulphate represented by the formula:



0.2 mol of N-β-diethylaminoethyl,N-[(3-nitro-4-methylamino)phenyl],N'-[(2'-nitro-4'-methoxy)phenyl]ethylenediamine (i.e. 92 g), isolated in the usual way from the previously obtained monohydrochloride, are dissolved in 200 cm³ of chlorobenzene at ambient temperature. 0.24 mol of methyl sulphate (i.e. 30.24 g) are added a little at a time with cooling. After 15 minutes, 115 g of the expected quaternary salt, in the pure state and melting at 124°C, are filtered off.

EXAMPLE XV

Preparation of N-β-diethylaminoethyl,N-[(3-nitro-4-methylamino)phenyl],N'-[(4'-nitro)phenyl]ethylenediamine



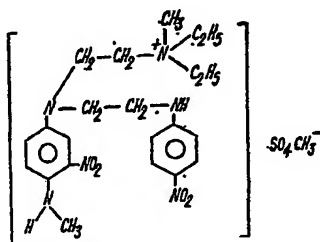
This product is obtained by condensing diethylaminoethyl chloride with the N-[(3-nitro-4-methylamino)phenyl],N'-[(4'-nitro)phenyl]ethylenediamine described in Example 1.

0.3 mol of N-[(3-nitro-4-methylamino)phenyl],N'-[(4'-nitro)phenyl]ethylenediamine, (i.e. 99 g), are dissolved in 2 litres of chlorobenzene under reflux. 1.5 mol of diethylaminoethyl chloride (i.e. 203 g) are added a little at a time with stirring, and refluxing is continued for four hours. The reaction mixture is cooled and the crude product is filtered off in the form of the monohydrochloride. The impure monohydrochloride is dissolved in 750 cm³ of 4N hydrochloric acid at 50°C. After cooling, the expected product is filtered off in the form of a practically pure dihydrochloride. This dihydrochloride, after treatment with 700 cm³ of a normal sodium hydroxide solution, yields 90 g of N-β-diethylaminoethyl,N-[(3-nitro-4-methylamino)phenyl],N'-[(4'-nitro)phenyl]ethylenediamine which after recrystallisation from ethyl alcohol melts at 132°C.

Analysis	Calculated for C ₂₁ H ₃₀ N ₆ O ₄	Found
C %	58.60	58.37 — 58.57
H %	6.97	7.20 — 6.98
N %	19.53	19.73 — 19.59

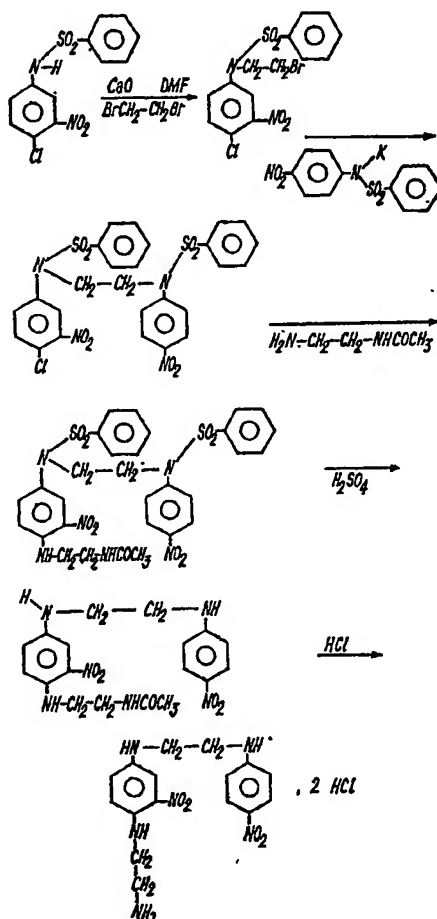
EXAMPLE XVI

Preparation of β-[N-[(3-nitro-4-methylamino)phenyl],N-β'-N'[(4'-nitro)phenyl]-aminoethyl]aminoethyl methyl diethyl ammonium methylsulphate represented by the formula:



0.14 mol of N-β-diethylaminoethyl,N-[(3-nitro-4-methylamino)phenyl],N'-[(4'-nitro)phenyl]ethylenediamine (i.e. 60 g) are dissolved in 600 cm³ of chlorobenzene at 50°C. 0.18 mol of methyl sulphate (i.e. 17 cm³) are added a little at a time with stirring and the reaction mixture is kept at 50°C for one hour. 78 g of the expected quaternary salt, which melts at 158°C, are filtered off.

EXAMPLE XVII
Preparation of N-[(3-nitro-4-β-aminoethylamino)phenyl],N'[(4'-nitro)-phenyl] ethylenediamine



5 First stage: preparation of 2-nitro-4-N-benzenesulphonyl,N-β-bromoethylamino-chlorobenzene. 5

0.5 mol of 2-nitro-4-N-benzenesulphonylamino-chlorobenzene (i.e. 156.25 g) are dissolved in 935 cm³ of dimethylformamide which has beforehand been heated to 95°C. 1.25 mol of quicklime (i.e. 70 g) are added and then 1.25 mol of dibromethane (i.e. 216 cm³) are added very rapidly. After heating for one hour on a boiling water bath the reaction mixture is filtered hot. 1 litre of iced water is added to the cooled filtrate. A very thick oil settles out. The supernatant liquid phase is removed, the oil is taken up in an aqueous alcohol mixture and 180 g of crystalline 2-nitro-4-N-benzenesulphonyl,N-β-bromomethylamino-chlorobenzene melting at 80°C are filtered off. 10

Second stage: preparation of N,N'-benzenesulphonyl,N-[(3-nitro-4-chloro)phenyl],-N'-[(4'-nitro)phenyl]ethylenediamine.

0.05 mol of 2-nitro-4-N-benzenesulphonyl,N-β-bromethylamino-chlorobenzene (i.e. 20.97 g) are dissolved in 150 cm³ of dimethylformamide which has beforehand been heated to 120°C. 0.1 mol of the potassium derivative of N-benzenesulphonyl-p-nitraniline (i.e. 31.6 g) are added and the reaction mixture is kept for one hour at 120°C and is then filtered hot. 150 cm³ of water are added to the cooled filtrate. A thick oil settles out. The supernatant solution is decanted, the oily residue is taken up in a mixture of acetone/alcohol, and 17 g of the expected product are filtered off and washed with normal sodium hydroxide solution, and then with water. After recrystallisation from acetic anhydride, 15 g of pure N,N'-benzenesulphonyl,N-[(3-nitro-4-chloro)phenyl],N'-[(4'-nitro)phenyl]ethylenediamine melting at 198°C are obtained.

Analysis	Calculated for C ₂₀ H ₂₁ S ₂ O ₆ N ₄ Cl	Found
N %	9.08	9.12 — 9.02
S %	10.38	10.38 — 10.47

Third stage: preparation of N,N'-benzenesulphonyl,N-[(3-nitro-4-β-acetaminoethyl-amino)phenyl],N'-[(4'-nitro)phenyl]ethylenediamine.

0.01 mol of N,N'-benzenesulphonyl,N-[(3-nitro-4-chloro)phenyl],N'-[(4'-nitro)phenyl]ethylenediamine (i.e. 6.16 g) in 0.1 mol of ethylenediamine monoacetate (i.e. 10 g) are heated at 140°C for 2 hours. The reaction mixture is poured onto 100 cm³ of iced water. 4.2 g of the expected product are filtered off, washed with a normal hydrochloric acid solution, then with water and finally with a little alcohol; after recrystallisation from a mixture of acetic acid/water the product melts at 185°C.

Analysis	Calculated for C ₃₀ H ₃₀ N ₆ O ₈ S	Found
N %	12.31	12.34 — 12.47
S %	9.39	9.56 — 9.56

Fourth stage: preparation of N[(3-nitro-4-β-acetaminoethylamino)phenyl],N'-[(4'-nitro)phenyl]ethylenediamine.

0.01 mol of N,N'-benzenesulphonyl,N[(3-nitro-4-β-acetaminoethylamino)phenyl],N'-[(4'-nitro)phenyl]ethylenediamine (i.e. 6.82 g) are dissolved in 35 cm³ of concentrated sulphuric acid at between 15 and 20°C. The reaction mixture is kept at this temperature for 24 hours and then poured onto ice. The expected product is filtered off in the form of a sulphate. This sulphate, on treatment with a 2N sodium hydroxide solution yields 3.4 g of the corresponding base in the form of a chestnut-coloured product which is filtered off. This crude product is purified by dissolving it in hot 2N hydrochloric acid and by crystallising the monohydrochloride of N[(3-nitro-4-β-acetaminoethylamino)phenyl],N'-[(4'-nitro)phenyl]ethylenediamine by cooling; the base obtained by neutralisation of this product melts at 156°C.

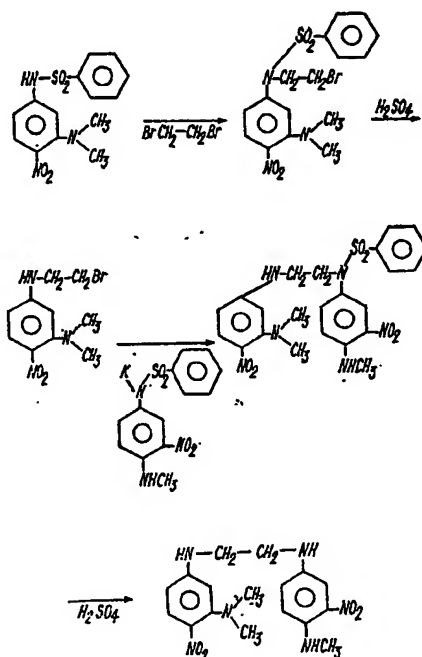
Analysis	Calculated for $C_{18}H_{22}N_6O_6$	Found
C %	53.73	53.71 — 53.91
H %	5.47	5.63 — 5.44
N %	20.89	20.68 — 20.65

Fifth stage: preparation of N-[(3-nitro-4-β-aminoethylamino)phenyl],N'-[(4'-nitro)-phenyl]ethylenediamine.

0.02 mol of N-[(3-nitro-4-β-acetaminoethylamino)phenyl],N'-[(4'-nitro)phenyl]-ethylenediamine (i.e. 8.04 g) are added to 45 cm³ of concentrated hydrochloric acid. The mixture is heated for 3 hours under reflux, cooled, 45 cm³ of absolute alcohol are added and the expected product is filtered off.

EXAMPLE XVIII

Preparation of N-[(4-nitro-3-dimethylamino)phenyl],N'-[(3'-nitro-4'-methyl-amino)phenyl]ethylenediamine



First stage: preparation of 1-N-benzene-sulphonylamino-3-dimethylamino-4-nitrobenzene.

0.1 mol of 1-amino-3-dimethylamino-4-nitrobenzene (i.e. 18.1 g) are dissolved in 90 cm³ of pyridine at 45°C. 0.1 mol of benzene-sulphonyl chloride (i.e. 14 cm³) are added gradually. The reaction mixture is kept at 45°C for 2 hours and is then poured onto 450 cm³ of iced water and acidified to pH=6 by means of hydrochloric acid. 30.7 g of the expected product, which melts at 153°C, are filtered off.

Second stage: preparation of 1-N-benzenesulphonyl,N-β-bromoethylamino-3-dimethylamino-4-nitrobenzene.

0.05 mol of 1-benzenesulphonylamino-3-dimethylamino-4-nitrobenzene (i.e. 16.05 g) are dissolved in 80 cm³ of dimethylformamide which has beforehand been heated to 95°C. 0.25 mol of quicklime (i.e. 14 g) are added and 0.15 mol of 1,2-dibromethane (i.e. 13 cm³) are then added very rapidly. After heating for one hour on a boiling water bath the hot reaction mixture is filtered. 400 cm³ of iced water are added to the cooled filtrate and 18.3 g of practically pure 1-N-benzenesulphonyl,N-β-bromomethylamino-3-dimethylamino-4-nitrobenzene which after recrystallisation from benzene melts at 121°C are filtered off.

Analysis	Calculated for C ₁₈ H ₁₈ N ₂ VS O ₄	Found
N %	9.81	10.01 — 9.95
S %	7.47	7.41 — 7.66

Third stage: preparation of 1 - N - β - bromoethylamino - 3 - dimethylamino - 4 - nitrobenzene.

0.16 mol of 1-N-benzenesulphonyl,N-β-bromomethylamino-3-dimethylamino-4-nitrobenzene (i.e. 68.48 g) are dissolved in 205 cm³ of concentrated sulphuric acid whilst keeping the temperature at 30°C. When dissolution is complete the reaction mixture is left for three hours at ambient temperature, then poured onto 1500 cm³ of iced water and rendered alkaline by means of a 5N sodium hydroxide solution. The expected product is extracted with ethyl acetate, the solvent is driven off in vacuo and 43.7 g of 1-N-β-bromomethylamino-3-dimethylamino-4-nitrobenzene are obtained in the form of a thick red oil.

Fourth stage: preparation of N-[(4 - nitro - 3 - dimethylamino)phenyl],N'-benzenesulphonyl,N'-[(3'-nitro-4'-methylamino)phenyl]ethylenediamine.

0.152 mol of the potassium derivative of 1-N-methylamino-2-nitro-4-N'-benzenesulphonylamino-3-dimethylamino-4-nitrobenzene (i.e. 52.5 g) are dissolved in 90 cm³ of dimethylformamide. 0.152 mol of 1-N-β-bromomethylamino-3-dimethylamino-4-nitrobenzene (i.e. 43.63 g) dissolved in 90 cm³ of dimethylformamide are added to this solution. The reaction mixture is heated for one hour at 80°C and is then cooled and poured into 2 litres of iced water. 65 g of the expected product are filtered off; after washing with water, with an 0.5 N sodium hydroxide solution and then with water, and drying the product melts at 138°C.

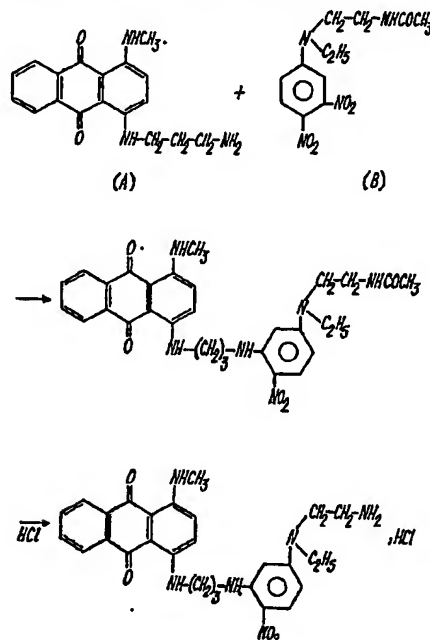
Fifth stage: preparation of N - [(4 - nitro - 3 - dimethylamino)phenyl],N' - [(3'-nitro-4'-methylamino)phenyl]ethylenediamine.

0.067 mol of N-[(4-nitro-3-dimethylamino)phenyl],N'-benzenesulphonyl,N'-[(3'-nitro-4'-methylamino)phenyl]ethylenediamine (34.5 g) are dissolved in 85 cm³ of concentrated sulphuric acid at between 35° and 40°C. The reaction mixture is kept at this temperature for five hours and is then left at ambient temperature for 24 hours. The mixture is poured onto 600 grams of ice, rendered alkaline by means of a sodium hydroxide solution, and the expected product is filtered off in the crude state. After washing with boiling alcohol this crude product yields 18 g of practically pure N-[(4-nitro - 3 - dimethylamino)phenyl],N' - [(3' - nitro - 4' - methylamino)phenyl]-ethylenediamine which after recrystallisation from chlorobenzene melts at 172°C.

Analysis	Calculated for $C_{17}H_{13}N_4O_4$	Found
C %	54.54	54.63 — 54.52
H %	5.88	5.84 — 5.91
N %	22.46	22.60 — 22.41

EXAMPLE XIX

Preparation of the monochlorohydrate of 1-methylamino- γ -[2'-nitro-N-ethyl-5'-N- β -aminoethylamino)phenyl]4-aminopropylaminoanthraquinone



First stage: Preparation of 1-methylamino- γ -[(2'-nitro-N-ethyl-5'-N-ethyl-5'-N- β -acetaminoethylamino)phenyl]4-aminopropylamino anthraquinone.

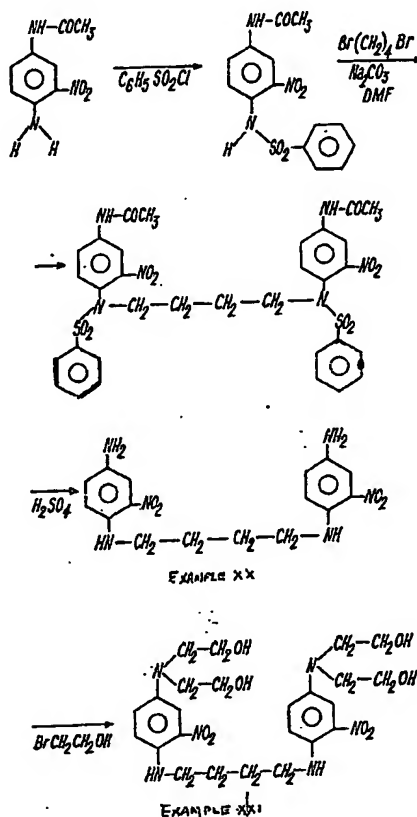
0.01 mole of 1-methylamino-4- γ -aminopropyl-anthraquinone (3.1 g.) and 0.005 mole (1.48 g.) of 3,4-dinitro-N-ethyl-N- β -acetaminoethyl aniline (m.p. = 129°C.), obtained by the nitration of N-ethyl-N- β -acetaminoethyl aniline with a sulphuric-nitric acid mixture, are refluxed for one hour in 20 cc. of pyridine. After cooling, the crude product is dried, and washed with a hydrochloric acid solution to remove the anthraquinone derivative starting material. 1.7 g. of practically pure product is obtained.

Second stage: Preparation of the monochlorohydrate of 1-methylamino- γ -[(2'-nitro-N-ethyl-5'-N- β -aminoethylamino)phenyl]4-aminopropylamino anthraquinone.

0.003 mole of 1-methylamino- γ -[(2'-nitro-N-ethyl-5'-N- β -acetaminoethylamino)phenyl]4-aminopropylamino anthraquinone (1.67 g.) is refluxed for 3 hours with 20 cc. of concentrated hydrochloric acid. After cooling the reaction mixture, 100 cc. of acetone is added and 0.8 g. of dried product is obtained.

EXAMPLES XX AND XXI

Preparation of N,N'-[(2-nitro-4-amino)phenyl]tetramethylenediamine and N,N'-[(2-nitro-4-di-β-hydroxyethylamino)phenyl]tetramethylenediamine



EXAMPLE XX

Preparation of N,N'-[(2-nitro-4-amino)phenyl]tetramethylenediamine.

First stage: Preparation of 1-benzenesulfonylamino-2-nitro-4-acetaminobenzene. This product is prepared in a known manner by reacting benzenesulphonyl chloride with 1-amino-2-nitro-4-acetaminobenzene dissolved in pyridine. After recrystallisation from alcohol the product melts at 199°C .

Second stage: Preparation of N,N'-benzenesulphonyl,N,N'[(2-nitro-4-acetamino)-phenyl]tetramethylenediamine.

2 mols of 1-benzenesulfonylamino-2-nitro-4-acetaminobenzene (i.e. 670 g) are dissolved in 2 litres of dimethylformamide which has beforehand been heated to 120°C . Whilst keeping the temperature at 120°C , 3 mols of anhydrous sodium carbonate (i.e. 318 g) are added to the reaction mixture followed by 1.5 mol of 1,4-dibromobutane (i.e. 179 cm³) added dropwise. After two hours heating the mixture is cooled, diluted five-fold with water, and the crude product is filtered off. This crude product is washed with 2 litres of boiling acetic acid. 694 g of practically pure N,N'-benzenesulphonyl,N,N'[(2-nitro-4-acetamino)phenyl]tetramethylenediamine, which melts at 296° with decomposition, are filtered off.

Third stage: Preparation of N,N'-[(2-nitro-4-amino)phenyl]tetramethylenediamine.

0.95 mol of N,N'-benzenesulphonyl,N,N'-[(2-nitro-4-acetamino)phenyl]tetramethylenediamine (i.e. 696 g) are gradually added with stirring and at between 0 and 10° to 2435 cm³ of concentrated sulphuric acid. The reaction mixture is left for 2 hours at ambient temperature and then 4850 cm³ of iced water are carefully added thereto, in such a way that the temperature does not exceed 95°. The N,N'-[(2-nitro-4-acetamino)phenyl]tetramethylenediamine precipitates. This product is not isolated but its suspension in dilute sulphuric acid is heated for 3 hours on a boiling water bath. After cooling, the expected product is filtered off in the form of a sulphate. After treatment with an ammonia solution this sulphate yields 283 g of N,N'-[(2-nitro-4-amino)phenyl]tetramethylenediamine which after recrystallisation from nitrobenzene and drying in vacuo at 100° melts at 240°.

Analysis	Calculated for C ₁₈ H ₂₀ N ₄ O ₄	Found
C %	53.33	53.45 — 53.45
H %	5.56	5.41 — 5.43
N %	23.33	23.46 — 23.21

EXAMPLE XXI

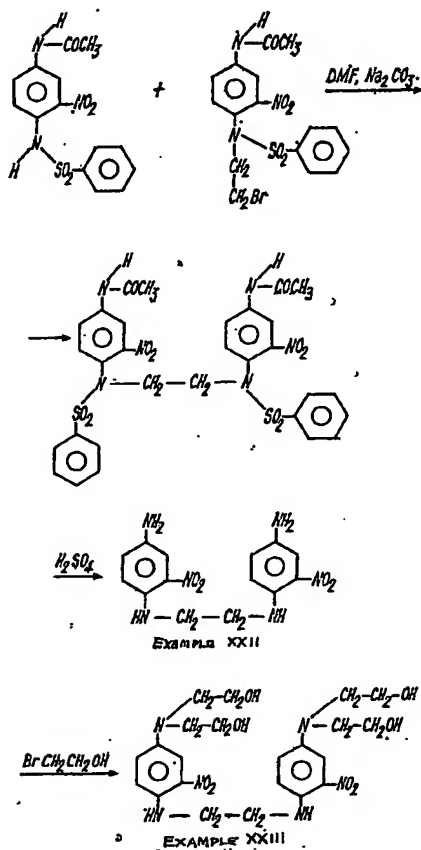
Fourth stage: Preparation of N,N' - [(2 - nitro - 4 - di - β - hydroxyethylamino)-phenyl]tetramethylenediamine.

0.7 mol of N,N' - [(2 - nitro - 4 - amino)phenyl]tetramethylenediamine (i.e. 250 g), prepared in Example I, are heated for 2 hours on a boiling water bath with 5.6 mols of 70% strength glycol bromhydrin (i.e. 1 kg) to which 250 cm³ of water, 250 cm³ of ethanol and 2.8 mols of calcium carbonate (i.e. 280 g) have been added. After cooling, the reaction mixture is poured into 2.5 litres of 4 N hydrochloric acid and cooled to 0°, and the expected product is filtered off in the form of a dihydrochloride. This dihydrochloride, after treatment with an ammonia solution, yields 283 g of N,N' - [(2 - nitro - 4 - di - β - hydroxymethylamino)phenyl]tetramethylenediamine which after recrystallisation from a mixture of methyl isobutyl ketone/ethyl alcohol melts at 144°.

Analysis	Calculated for C ₂₄ H ₃₄ N ₆ O ₈	Found
C %	53.73	53.61 — 53.76
H %	6.71	6.91 — 6.71
N %	15.67	15.53 — 15.59

EXAMPLES XXII AND XXIII

Preparation of N,N'-[(2-nitro-4-amino)phenyl]ethylenediamine and N,N'-[(2-nitro-4-di-β-hydroxyethylamino)phenyl]ethylenediamine.



EXAMPLE XXII

Preparation of N,N'-[(2-nitro-4-amino)phenyl]ethylenediamine.

First stage: Preparation of 1 - (N - benzenesulphonyl,N - β - bromoethyl)amino-2-nitro-4-acetaminobenzene.

0.7 mol of 1-benzenesulphonylamino-2-nitro-4-acetaminobenzene (i.e. 234.5 g) are added with stirring to 1250 cm³ of water to which 0.7 mol of lime (i.e. 39.2 g) have been added beforehand.

Stirring is continued for 3 hours and the calcium derivative is filtered off and dried in vacuo at 50°.

The calcium derivative previously obtained is dissolved in 1200 cm³ of dimethylformamide which has beforehand been heated on a boiling water bath. 1.4 mol of 1,2-dibromethane (i.e. 263 g) are added as rapidly as possible with good stirring and the reaction mixture is kept on a boiling water bath for 2 hours. After cooling and adding 2 litres of water, 290 g of 1-(N-benzenesulphonyl,N-β-bromoethyl)amino-2-nitro-4-acetaminobenzene are filtered off; after treatment with a N/2 sodium hydroxide solution in order to remove a little of the initial product, washing with water, drying and recrystallisation from acetic acid, the material melts at 153°.

Analysis	Calculated for $C_{18}H_{18}O_6N_4SBr$	Found
C %	43.43	43.65 — 43.64
H %	3.61	3.72 — 3.59
N %	9.50	9.76 — 9.50

Second stage: Preparation of N,N' -benzenesulphonyl, N,N' -[(2-nitro-4-acetamino)phenyl]ethylenediamine.

0.15 mol of 1-benzenesulphonylamino-2-nitro-4-acetaminobenzene (i.e. 50.25 g) are dissolved in 450 cm³ of dimethylformamide which has beforehand been heated to 90°. 0.225 mol of anhydrous sodium carbonate (23.85 g) followed by 0.15 mol of 1-(N-benzenesulphonyl,N-β-bromoethyl)amino-2-nitro-4-acetaminobenzene (i.e. 66.3 g) are added. The reaction mixture is heated for three hours at 120° and is then cooled and poured onto 2 litres of iced water. 64 g of a crude product are filtered off, washed with a N sodium hydroxide solution and then with water; after recrystallisation from a mixture of acetic acid and water and then from acetic acid, the material yields 40 g of practically pure N,N' -benzenesulphonyl, N,N' -[(2-nitro-4-acetamino)phenyl]ethylenediamine which melts at 248°.

Third stage: Preparation of N,N' -[(2-nitro-4-amino)phenyl]ethylenediamine.

0.09 mol of N,N' -benzenesulphonyl, N,N' -[(2-nitro-4-acetamino)phenyl]ethylenediamine (i.e. 62.64 g) are dissolved in 250 cm³ of concentrated sulphuric acid at 25°. The reaction mixture is left at this temperature for 2 hours and then 500 cm³ of iced water are carefully added to it in such a way that the temperature of the mixture does not exceed 95°. The reddish orange N,N' -[(2-nitro-4-acetamino)phenyl]ethylenediamine precipitates. This product is not isolated, but its suspension in dilute sulphuric acid is heated for 3 hours on a boiling water bath. After cooling, the expected product is filtered off in the form of a yellow sulphate. This sulphate, after treatment with an ammonia solution, yields 28 g of N,N' -[(2-nitro-4-amino)phenyl]ethylenediamine which after recrystallisation from nitrobenzene and drying in vacuo at 100° melts at 235°.

Analysis	Calculated for $C_{14}H_{16}N_4O_4$	Found
C %	50.60	50.40 — 50.50
H %	4.82	4.96 — 4.85
N %	19.28	19.47 — 19.33

EXAMPLE XXIII

Fourth stage: Preparation of N,N' -[(2-nitro-4-di-β-hydroxyethylamino)phenyl]ethylenediamine.

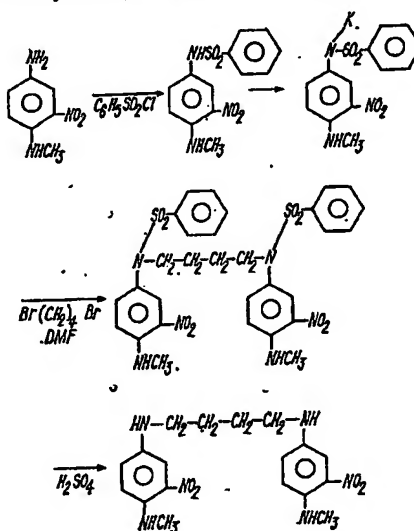
0.01 mol of N,N' -[(2-nitro-4-amino)phenyl]ethylenediamine (i.e. 3.2 g) are heated for 2 hours on a boiling water bath with 0.08 mol of glycol bromhydrin (i.e. 14.3 g of 70% strength material) to which 3 cm³ of water, 3 cm³ of alcohol and 0.04

5 mol of calcium carbonate (i.e. 4 g) have been added. The reaction mixture is cooled and then poured on to 30 cm³ of 5 N hydrochloric acid cooled in a mixture of ice and salt. About 1 g of a hydrochloride which is not the expected product is removed by filtration. The filtrate is rendered alkaline with an ammonia solution and 2.5 g of N,N' - [2 - nitro - 4 - di - β - hydroxyethylamino]phenyl]ethylenediamine which after recrystallisation from a mixture of ethanol and water melts at 196° are filtered off.

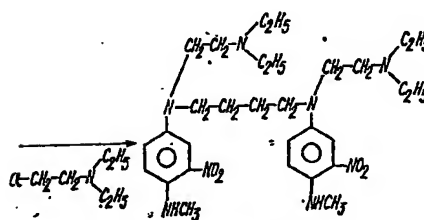
Analysis	Calculated for $C_{22}H_{22}N_8O_8$	Found
C %	51.97	52.17 — 52.19
H %	6.30	6.55 — 6.41
N %	16.53	16.39 — 16.29

EXAMPLES XXIV AND XXV

10 Preparation of N,N' - [(3-nitro-4-methylamino)phenyl]tetramethylenediamine and of the tetrahydrochloride of N,N' - β -diethylaminoethyl, N,N' - [(3-nitro-4-methylamino)phenyl]tetramethylenediamine.



Example XXIV



Example XXV

EXAMPLE XXIV

Preparation of N,N'-[(3-nitro-4-methylamino)phenyl]tetramethylenediamine.

First stage: Preparation of N,N'-benzenesulphonyl,N,N'-[(3-nitro-4-methylamino)phenyl]tetramethylenediamine.

0.6 mol (i.e. 207 g) of the potassium derivative of 1-N-methylamino-2-nitro-4-N'-benzenesulphonylaminobenzene, whose preparation is described in British Specification No. 1,164,824, are dissolved in 600 cm³ of dimethylformamide which has before-hand been heated to 95°. Whilst keeping the reaction mixture at this temperature throughout, 0.315 mol of 1,4-dibromobutane (i.e. 37.6 cm³) are added dropwise. The mixture is heated for a further 45 minutes, cooled, and 170 g of N,N'-benzenesulphonyl,N,N'-[(3-nitro-4-methylamino)phenyl]tetramethylenediamine, which after recrystallisation from dimethylformamide melts at 245°, are filtered off.

Analysis	Calculated for C ₂₀ H ₂₂ O ₂ N ₄ S ₂	Found
C %	53.88	53.78 — 53.70
H %	4.79	4.93 — 4.97
N %	12.27	12.45 — 12.40

Second stage: Preparation of N,N'-[(3-nitro-4-methylamino)phenyl]tetramethylenediamine.

0.252 mol of N,N'-benzenesulphonyl,N,N'-[(3-nitro-4-methylamino)phenyl]tetramethylenediamine (i.e. 168 g) are dissolved in 750 cm³ of concentrated sulphuric acid cooled in an ice bath. When dissolution is complete the reaction mixture is left for 24 hours at ambient temperature and then poured onto 8 kg of ice. The expected product, which has precipitated in the form of a sulphate, is filtered off. This sulphate is treated with 500 cm³ of pyridine on a boiling water bath. After cooling, 89 g of N,N'-[(3-nitro-4-methylamino)phenyl]tetramethylenediamine are filtered off and washed with water; after one recrystallisation from pyridine the material melts at 210°.

EXAMPLE XXV

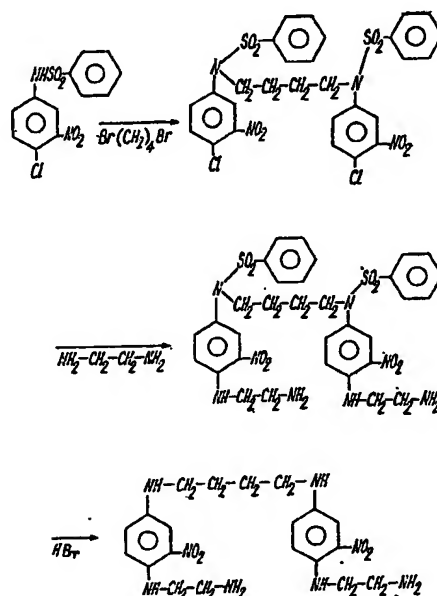
Third stage: Preparation of the tetrahydrochloride of N,N'-β-diethylaminoethyl,N,N'-[(3-nitro-4-methylamino)phenyl]tetramethylenediamine.

0.245 mol of N,N'-[(3-nitro-4-methylamino)phenyl]tetramethylenediamine (i.e. 95 g) are dissolved in 950 cm³ of chlorobenzene under reflux. 2.45 mols of diethylaminoethyl chloride (i.e. 332 g) are added gradually and the reaction mixture is kept under reflux for three hours. The mixture is cooled to 0° and the expected product, which is in the form of an impure dihydrochloride, is rapidly filtered. This crude product is taken up in a sufficient amount of 2 N sodium hydroxide solution and the desired product is extracted with methyl isobutyl ketone. The solution of methyl isobutyl ketone is dried over sodium sulphate, filtered and then evaporated in vacuo. The oily residue is dissolved in propanol. After bubbling hydrochloric acid gas into the ice-cooled propanol solution, 111 g of a tetrahydrochloride of N,N'-β-diethylaminoethyl,N,N'-[(3-nitro-4-methylamino)phenyl]tetramethylenediamine are filtered off; after recrystallisation from a mixture of ethanol and concentrated hydrochloric acid this material melts at about 150° with decomposition.

Analysis	Calculated for $C_{20}H_{24}O_4N_8Cl_4$	Found
C %	49.18	49.27 — 49.20
H %	7.38	7.68 — 7.50
N %	15.30	15.14 — 15.22

EXAMPLE XXVI

Preparation of N,N'-[(3-nitro-4-β-aminoethylamino)phenyl]tetramethylenediamine



5 First stage: Preparation of N,N' - benzenesulphonyl,N,N' - [(3 - nitro - 4 - chloro)-phenyl]tetramethylenediamine. 5

0.16 mol of 2-nitro-4-benzenesulphonylamino-chlorobenzene (i.e. 50 g) are dissolved in 400 cm³ of dimethylformamide which has been heated beforehand on a boiling water bath; 0.4 mol of 95% pure quicklime (i.e. 23.6 g) are added followed dropwise by 0.14 mol of 1,4-dibromobutane (i.e. 16.7 cm³) whilst keeping the reaction mixture on a boiling water bath throughout. After two hours heating the mixture is cooled, 100 cm³ of water are added and 40 g of N,N'-benzenesulphonyl,N,N'-[(3-nitro-4-chloro)phenyl]tetramethylenediamine are filtered off; after recrystallisation from acetic acid this material melts at 193°C. 10

Analysis	Calculated for $C_{25}H_{24}O_8N_4S_2Cl_2$	Found
N %	8.25	8.39 — 8.49
S %	9.42	9.47 — 9.32

Second stage: Preparation of N,N' - benzenesulphonyl,N,N' - [(3 - nitro - 4 - β -aminoethylamino)phenyl]tetramethylenediamine.

0.027 mol of N,N' - benzenesulphonyl,N,N' - [(3 - nitro - 4 - chloro)phenyl]-tetramethylenediamine (i.e. 18.3 g) are dissolved in 0.44 mol of ethylenediamine monohydrate (i.e. 23 cm³) heated to 95° beforehand. The reaction mixture is kept for 30 minutes on a boiling water bath, cooled and poured into 350 cm³ of water with stirring. 20 g of N,N' - benzenesulphonyl,N,N' - [(3 - nitro - 4 - β - aminoethylamino)phenyl]tetramethylenediamine are filtered off, washed with water and dried in vacuo; after recrystallisation from propanol and drying in vacuo at 90° the material melts at 160°.

Analysis	Calculated for $C_{32}H_{38}O_8N_6S_2$	Found
N %	15.43	15.45 — 15.60
S %	8.83	8.81 — 8.93

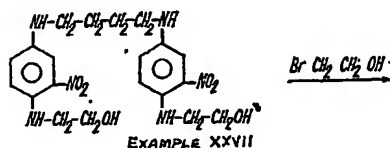
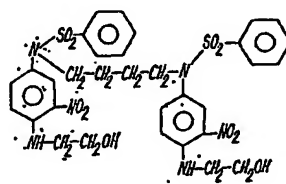
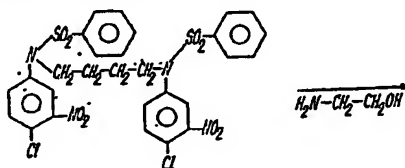
Third stage: Preparation of N,N' - [(3 - nitro - 4 - β - aminoethylamino)phenyl]-tetramethylenediamine.

0.161 mol of N,N'-benzenesulphonyl,N,N'-[(3-nitro-4- β -aminoethylamino)-phenyl]tetramethylenediamine (i.e. 117 g) are introduced into 1170 cm³ of 48% strength hydrobromic acid and the mixture is heated under reflux for 45 minutes. The reaction mixture is cooled to -10°, 1000 cm³ of absolute ethanol are added, and 68 g of the expected product are filtered off in the form of a tetrahydrobromide. This tetrahydrobromide is treated with a 2 N sodium hydroxide solution, and N,N' - [(3 - nitro - 4 - β - aminoethylamino)phenyl]tetramethylenediamine is filtered off, washed with water and dried in vacuo at 90°; after recrystallisation from chlorobenzene the material melts at 195°.

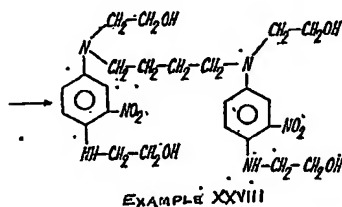
Analysis	Calculated for $C_{20}H_{30}N_6O_4$	Found
C %	53.81	54.00 — 53.92
H %	6.73	6.76 — 6.69
N %	25.11	25.30 — 25.28

EXAMPLES XXVII AND XXVIII

Preparation of N,N'-[(3-nitro-4-β-hydroxyethylamino)phenyl]tetramethylenediamine and N,N'-[(3-nitro-4-β-hydroxyethylamino)phenyl],N,N'-β-hydroxyethyltetramethylenediamine.



EXAMPLE XXVII



EXAMPLE XXVIII

EXAMPLE XXVII

Preparation of N,N'-[(3-nitro-4-β-hydroxyethylamino)phenyl]-tetramethylenediamine.

First stage: Preparation of N,N'-benzenesulphonyl,N,N'-[(3-nitro-4-β-hydroxyethylamino)phenyl]tetramethylenediamine.

0.256 mol of N,N'-benzenesulphonyl,N,N'-[(3-nitro-4-β-hydroxyethylamino)phenyl]tetramethylenediamine prepared according to the process described in the preceding Example (i.e. 174 g) are added with stirring to 7.68 mols of ethanolamine (i.e. 468 g) which has beforehand been heated to 120°, the addition being so controlled as to keep the reaction at between 120 and 130°, the reaction being exothermic. When the reaction is complete the reaction mixture is cooled and poured into 3 litres of water. The expected product is filtered off, washed with normal hydrochloric acid solution and then with water and dried in vacuo at 90°. After recrystallisation from dioxane and drying in vacuo at 90°, the material melts at 165°.

Analysis	Calculated for $C_{22}H_{28}O_{10}N_8S_2$	Found
N %	11.53	11.63 — 11.61
S %	8.79	8.80 — 8.93

Second stage: Preparation of N,N' - [(3 - nitro - 4 - β - hydroxyethylamino)-phenyl]tetramethylenediamine.

0.2 mol of N,N' -benzenesulphonyl, N,N' -[(3-nitro-4- β -hydroxyethylamino)-phenyl]tetramethylenediamine (i.e. 152 g) are dissolved gradually with stirring in 1500 cm³ of concentrated hydrochloric acid heated beforehand to 85°. The reaction mixture is heated for 45 minutes on a boiling water bath, then cooled to -10°, and the expected product is filtered off in the form of a hydrochloride. This hydrochloride, after treatment with an ammonia solution, yields 68 g of N,N' -[(3-nitro-4- β -hydroxyethylamino)phenyl]tetramethylenediamine which after recrystallisation from nitrobenzene and drying in vacuo melts at 210°.

Analysis	Calculated for $C_{20}H_{28}O_6N_8$	Found
C %	53.57	53.67 — 53.70
H %	6.25	6.09 — 6.13
N %	18.75	18.70 — 18.75

EXAMPLE XXVIII

Third stage: Preparation of N,N' - [(3 - nitro - 4 - β - hydroxyethylamino)-phenyl] N,N' - β -hydroxyethyl-tetramethylenediamine.

0.1 mol of N,N' - [(3 - nitro - 4 - β - hydroxyethylamino)phenyl]tetramethylenediamine (i.e. 44.8 g) are heated for two hours on a boiling water bath with 0.8 mol of glycol bromhydrin (i.e. 108 g) to which 20 cm³ of water, 25 cm³ of ethanol and 40 g of calcium carbonate have been added. The mixture is cooled and 400 cm³ of water are added. A very thick oil settles out. The supernatant liquid phase is decanted and the oil is dissolved in 500 cm³ of chloroform. The chloroform solution is carefully washed with water, dried over sodium sulphate, filtered, cooled to 0°, and saturated with dry hydrogen chloride. 56 g of the expected product are filtered off in the form of a dihydrochloride. This dihydrochloride, on treatment with a N sodium hydroxide solution, yields N,N' -[(3-nitro-4- β -hydroxyethylamino)phenyl] N,N' - β -hydroxyethyl-tetramethylenediamine, initially in the form of a thick oil which however crystallises easily in a mixture of chloroform and methanol. After recrystallisation from this same mixture of solvents the product melts at 108°.

Analysis	Calculated for $C_{24}H_{30}N_8O_6$	Found
C %	53.73	53.77 — 53.77
H %	6.71	6.68 — 6.54
N %	15.67	15.58 — 15.65

USE EXAMPLES

EXAMPLE XXIX

The following dyeing composition is prepared:

5	N-[(2-nitro-4-di-β-hydroxyethylamino)phenyl], N'-[(4'-nitro)phenyl]ethylenediamine	0.2 g 15 g	5
	2-butoxyethanol		
	sodium carbonate q.s.p. pH 9	100 g	
	water q.s.p.		

10 This composition is applied to bleached hair. It is allowed to act for 15 minutes and the hair is then rinsed and shampooed. A MATT ASH BLONDE is obtained. 10

EXAMPLE XXX

The following dyeing composition is prepared:

15	[1-methylamino-4-[γ-(2'-nitro-5'-trimethylammonium)phenyl]aminopropylamino-anthraquinone]methylsulphate	3 g	15
	20% strength ammonia q.s.p. pH 8	100 g	
	water q.s.p.		

When this solution is applied to hair which is 90% white, it gives a green shade after 30 minutes application, rinsing and shampooing.

EXAMPLE XXXI

The following dyeing composition is prepared:

25	N-[(2-nitro-4-β-diethylmethylammonium-ethylamino)phenyl], N'-[(4'-nitro)phenyl]-ethylenediamine	0.56 g	25
	Lauryl alcohol oxethylated with 10.5 mols of ethylene oxide per mole of alcohol	1 g	
	2-normal Na ₂ CO ₃ solution, q.s.p. pH=9	100 g	
	water q.s.p.		

30 This composition as applied to hair which is 90% white, allowed to act for 15 minutes, and the hair is rinsed and shampooed. A REDDISH BLONDE is obtained. 30

EXAMPLE XXXII

The following dyeing composition is prepared:

35	N-[(2-nitro-4-β-aminoethylamino)phenyl], N'-[(4'-nitro)phenyl]ethylenediamine	0.4 g	35
	lauryl alcohol oxethylated with 10.5 mols of ethylene oxide per mole of alcohol	1 g	
	2-normal Na ₂ CO ₃ solution q.s.p. pH=9	100 g	
	water q.s.p.		

40 This composition is applied to hair which is 90% white, allowed to act for 15 minutes, and the hair rinsed and shampooed. A STRONG MAHOGANY colour is obtained. 40

EXAMPLE XXXIII

The following dyeing composition is prepared:

45	N[(3-nitro-4-methylamino)phenyl], N-β-[(3'-nitro-4-methylamino)phenyl]aminoethyl, N,N-dimethylammonium iodide	0.5 g	45
	normal Na ₂ CO ₃ solution q.s.p. pH=8	100 g	
	water q.s.p.		

50 This composition is applied to 100% white hair. It is allowed to act for 20 minutes and the hair rinsed and shampooed. A slightly ASHEN CHESTNUT colour is obtained. 50

EXAMPLE XXXIV

The following dyeing composition is prepared:

5	β -[N-[(3-nitro-4-methylamino)phenyl], N- β '-N'- [4'-nitro)phenyl] aminoethyl] aminoethyl methyl diethyl ammonium methylsulphate	0.56 g 5 g	5
	isooctylphenyl polyethoxyethanol		
	Na ₂ CO ₃ , q.s.p. pH = 7.5	100 g	
	water, q.s.p.		

10 This composition is applied to hair which is 90% white, allowed to act for 15
minutes, and the hair rinsed and shampooed. 10
A slightly REDDISH BLONDE is obtained.

EXAMPLE XXXV

The following dyeing composition is prepared:

15	β -[N-[(3-nitro-4-methylamino)phenyl], N- β '-N'- [(4'-nitro)phenyl] aminoethyl] aminoethyl methyl diethyl ammonium methylsulphate	0.45 g	15
	4-N- γ -aminopropylamino-1-N'-methyl- amino-anthraquinone	0.05 g 4 g	
20	isooctylphenyl polyethoxyethanol		20
	lauryl alcohol oxyethylated with 10.5 mols of ethylene oxide per mole of alcohol	1 g	
	Na ₂ CO ₃ , q.s.p. pH = 9	100 g	
	water, q.s.p.		

25 This composition is applied to hair which is 90% white, allowed to act for 15
minutes, and the hair rinsed and shampooed. A NEUTRAL GREY is obtained. 25

EXAMPLE XXXVI

The following dyeing composition is prepared:

30	N-diethylaminoethyl, N-[(3-nitro-4-methylamino)- phenyl], N'-[(4'-nitro)phenyl] ethylenediamine monohydrochloride	0.5 g 5 g	30
	isooctylphenyl polyethoxyethanol		
	2 N solution of Na ₂ CO ₃ , q.s.p. pH = 7.5	100 g	
	water, q.s.p.		

35 This composition is filtered. The filtrate is applied to hair which has been bleached
to a platinum shade, is allowed to act for 20 minutes, and the hair is shampooed and
rinsed. 35
A REDDISH BLONDE is obtained.

EXAMPLE XXXVII

The following dyeing composition is prepared:

40	N- β -diethylaminoethyl, N-[(3-nitro-4-methyl- amino)phenyl], N'-[(4'-nitro)phenyl] ethylene- diamine monohydrochloride	0.5 g	40
	1-diethylaminoethylamino-2-nitro-4-N,N- dihydroxyethylamino-benzene dihydrochloride	0.04 g 4.5 g	
45	isooctylphenyl polyethoxyethanol		45
	2N solution of Na ₂ CO ₃ , q.s.p. pH = 7.5	100 g	
	water, q.s.p.		

50 This composition is filtered and the filtrate applied to hair which has been bleached
to a platinum shade, allowed to act for 15 minutes, and the hair rinsed and shampooed.
A rather strong PEARLY BEIGE is obtained. 50

EXAMPLE XXXVIII

The following dyeing composition is prepared:

5	β -[N-[(3-nitro-4-methylamino)phenyl], N- β '-N'-		
	[(2'-nitro-4'-methoxy)phenyl]aminoethyl]amino-		
	ethyl methyl diethyl ammonium methylsulphate	0.58 g	5
	isooctylphenyl polyethoxyethanol	5 g	
	2 N solution of Na_2CO_3 , q.s.p. pH=9		
	water, q.s.p.	100 g	

10 This composition is applied to light chestnut hair, allowed to act for 10 minutes, and the hair rinsed and shampooed. A LIGHT MAHOGANY CHESTNUT is obtained.

EXAMPLE XLIX

The following dyeing composition is prepared:

15	β -[N-[(3-nitro-4-methylamino)phenyl], N- β '-N'-		
	[(4'-nitro)phenyl]aminoethyl]aminoethyl methyl diethyl		
	ammonium methylsulphate	0.56 g	15
	isooctylphenyl polyethoxyethanol	5 g	
	2 N solution of Na_2CO_3 , q.s.p. pH=7.5		
	water, q.s.p.	100 g	

20 This composition is applied to hair which is 90% white, allowed to act for 15 minutes, and the hair rinsed and shampooed. A REDDISH BLONDE is obtained.

EXAMPLE XL

The following dyeing composition is prepared:

25	N,N'-[(3-nitro-4- β -aminoethylamino)phenyl]		
	tetramethylenediamine tetrahydrobromide	0.77 g	
	isooctylphenyl polyethoxyethanol	5 g	25
	2 N solution of Na_2CO_3 , q.s.p. pH 7		
	water, q.s.p.	100 g	

30 This composition is applied to chestnut hair, allowed to act for 10 minutes, and the hair shampooed and rinsed. A deepening of the shade, with a VIOLINE MAHOGANY sheen, is obtained.

EXAMPLE XLI

The following dyeing composition is prepared:

35	N,N'-[(3-nitro-4- β -aminoethylamino)phenyl]		
	tetramethylenediamine tetrahydrobromide	0.08 g	
	β -[N-(2-nitro-4-N'-methyl, N'-benzenesulphonyl-		
	amino-phenyl)]aminoethyl methyl diethyl ammonium		
	methylsulphate	0.48 g	35
	isooctylphenyl polyethoxyethanol	5 g	
	2 N solution of Na_2CO_3 , q.s.p. pH 7		
40	water, q.s.p.	100 g	40

This composition is applied to hair which is 90% white, allowed to act for 15 minutes, and the hair is shampooed and rinsed. A GOLDEN REDDISH BLONDE is obtained.

EXAMPLE XLII

The following dyeing composition is prepared:

	Coprah diethanolamide	3 g	
	sodium lauryl sulphate oxethylated with 2 moles of ethylene oxide per mole of lauryl compound, containing 19% of lauryl alcohol	4 g	5
5	2-butoxyethanol	4 g	
	isooctylphenyl polyethoxyethanol	5 g	
	N,N'-bis[(2'-nitro-4'-bis-β-hydroxyethylamino)phenyl]tetramethylenediamine	0.43 g	10
10	4-nitro-1,3-diamino-benzene monoethanolamine q.s.p. pH 8	100 g	
	water, q.s.p.		

This composition is applied to hair which has been bleached to a platinum shade, allowed to act for 15 minutes, and the hair shampooed and rinsed.
A PEARLY BIEGE is obtained.

f5

EXAMPLE XLIII

The following dyeing composition is prepared:

	N,N'-di-β-hydroxyethyl, N,N'-di-[(3'-nitro-4-β-hydroxyethylamino)phenyl]tetramethylenediamine	0.6 g	
	isooctylphenyl polyethoxyethanol	5 g	20
20	2-butoxyethanol	10 g	
	2 N solution of Na ₂ CO ₃ , q.s.p. pH 9	100 g	
	water, q.s.p.		

This solution is applied to hair which has been very strongly bleached, allowed to act for 15 minutes, and the hair shampooed and rinsed.
A PLATINUM sheen is obtained.

25

EXAMPLE XLIV

The following dyeing composition is prepared:

	N,N'-bis-diethylaminoethyl, N,N'-bis-[(4-methylamino-3-nitro)phenyl]tetramethylenediamine	0.73 g	30
30	isooctylphenyl polyethoxyethanol	5 g	
	2 N solution of Na ₂ CO ₃ , q.s.p. pH = 7.5	100 g	
	water, q.s.p.		

This solution is applied to hair which is 90% white, allowed to act for 15 minutes, and the hair shampooed and rinsed.
A LIGHT VIOLET is obtained.

35

EXAMPLE XLV

The following dyeing composition is prepared:

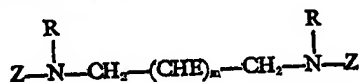
	1-methylamino-γ-[(2'-nitro-N-ethyl-5'-N-β-aminoethylamino)phenyl]4-aminopropylamino anthraquinone monochloride	3 g	40
40	20% NH ₃ q.s.p. pH = 7.9	100 g	
	water, q.s.p.		

This solution is applied to hair which is 90% white, allowed to act for 30 minutes at 35°C., and the hair rinsed and shampooed.
A GREEN colour is obtained.

45

WHAT WE CLAIM IS:—

1. Compounds of the formula:



I

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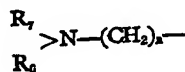
wherein each of the Z radicals, which may be the same or different, represents a nitrobenzene or anthraquinone radical, at last one of which Z radicals being substituted by an amino radical, which is unsubstituted or substituted by one or two alkyl, hydroxyalkyl, amino alkyl, monoalkylaminoalkyl or dialkylaminoalkyl radicals, the alkyl radicals in the said substituents containing 1 to 4 carbon atoms, or by an alkyl or alkoxy radical containing 1 to 4 carbon atoms, E represents a hydrogen atom or hydroxy radical;

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5

10

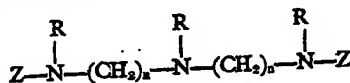


wherein n is 2, 3, 4, 5 or 6; and each of R₇ and R₆, which may be the same or different, represents a hydrogen atom or an alkyl radical containing 1 to 4 carbon atoms, subject to the proviso that at least one of R₇ and R₆ represents a said alkyl radical, or R₇ and R₆ together with the nitrogen atom to which they attached form a heterocyclic ring, with the proviso that when E represents a hydroxyl radical m is not 2, and acid addition salts and quaternary ammonium salts thereof.

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15

2. Compounds of the formula:



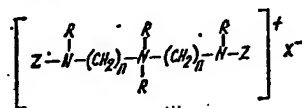
II

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wherein Z, and R and each of the n values which may be the same or different are as defined in claim 1 and acid addition salts and quaternary ammonium salts thereof.

20

3. Compounds according to claim 2 having the formula



III

25

wherein X represents a halogen atom.

25

4. Compounds according to any of claims 1 to 3 in which at least one of the Z radicals represents a phenyl radical substituted by a nitro radical.

5. Compounds according to any of claims 1 to 4 in which at least one of the Z radicals represents an anthraquinone radical.

30

6. Compounds according to any one of claims 1 to 5 wherein E represents a hydrogen atom, one of the R radicals does not represent an alkyl radical of 1 to 4 carbon atoms and at least one of the Z radicals represents a nitrophenyl radical which is substituted by an amino radical which is unsubstituted or substituted by one or two alkyl, hydroxyalkyl or aminoalkyl radicals, of 1 to 4 carbon atoms, or an anthraquinone radical substituted by an amino radical which is unsubstituted or substituted by one or two alkyl radicals of 1 to 4 carbon atoms.

30

35

7. Compounds according to claim 6 wherein one of the Z radicals represents a nitrophenyl radical substituted by an alkoxy radical of 1 to 4 carbon atoms, and the other Z radical is a nitrophenyl radical substituted by an amino radical which is unsubstituted or substituted by one or two alkyl, hydroxyalkyl or aminoalkyl radicals of 1 to 4 carbon atoms.

35

40

8. Compounds according to any one of claims 1 to 4 wherein R does not represent an alkyl radical of 1 to 4 carbon atoms and at least one of the Z radicals represents a nitrophenyl radical substituted by an amino radical which is unsubstituted or substituted by one or two alkyl, hydroxyalkyl or aminoalkyl radicals of 1 to 4 carbon atoms.

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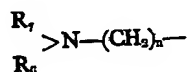
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9. A compound according to claim 6 specifically identified in any one of Examples I to XI.

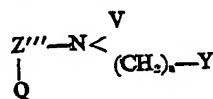
10. A compound according to claim 6 or 7 specifically identified in any one of Examples XII to XIX.

11. A compound according to claim 8 specifically identified in any one of Examples XX to XXVIII.

12. Process for preparing a compound of formula I, II or III as set out in claims 1, 2 and 3, in which each of the Z radicals, which may be the same or different, represents a nitrobenzene or anthraquinone radical, at least one of which Z radicals being substituted by an amino radical, which is unsubstituted or substituted by one or two alkyl, hydroxyalkyl, amino alkyl, monoalkylaminoalkyl or dialkylaminoalkyl radicals, the alkyl radicals in the said substituents containing 1 to 4 carbon atoms, or by an alkyl or alkoxy radical containing 1 to 4 carbon atoms; E represents a hydrogen atom or a hydroxyl radical; m is 0, 1, 2, 3 or 4; and each of the R radicals, which may be the same or different, represents a hydrogen atom, an alkyl or hydroxy-alkyl radical containing 1 to 4 carbon atoms or a radical of the formula

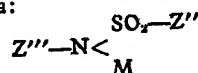


wherein n is 2, 3, 4, 5 or 6; and each of R₁ and R₂, which may be the same or different, represents a hydrogen atom, or an alkyl radical containing 1 to 4 carbon atoms, subject to the proviso that at least one of R₁ and R₂ represents a said alkyl radical, or R₁ and R₂ together with the nitrogen atom to which they are attached for a heterocyclic ring, and X represents a halogen atom, which comprises condensing a compound of the formula



in which Y represents a halogen atom, an alkali metal or alkaline earth metal atom, or a primary, secondary or tertiary amine group, Q represents a hydrogen or halogen atom such as chlorine or bromine, V is the same as R, defined in claim 1, or represents the radical SO₂-Z'' in which Z'' represents a phenyl or tolyl radical, with

(i) a compound of the formula:

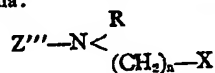


IV

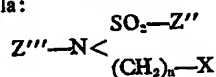
if Y represents a halogen atom;
(ii) a compound of the formula:



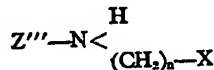
in which Q₁ represents a mobile group, such as a nitro group or halogen atom, which is readily substituted by an amino group if Y represents a primary amino group;
(iii) a compound of the formula:



if Y represents a secondary or tertiary amino group;
(iv) a compound of the formula:



or of the formula:



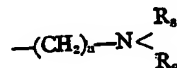
if Y represents an alkali metal or alkaline earth metal and n in formula IV is 0, and hydrolysing the SO₂-Z'' group;

- 40

and, optionally reacting the resulting compound so as to replace Q by a radical of the formula:



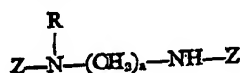
5 in which R_6 represents a hydrogen atom, an alkyl, hydroxyalkyl or alkoxyalkyl group, the alkyl groups of which substituents containing 1 to 4 carbon atoms, or a radical of the formula:



10 in which each of R_7 and R_8 , which may be the same or different, represents a hydrogen atom, or an alkyl or hydroxyalkyl radical of 1 to 4 carbon atoms or an acetyl radical or, together with the nitrogen atom to which they are attached, form a heterocyclic ring,

15 in which Z''' is the same as, or is a radical capable of being converted during the course of the reaction into, Z and when Z''' is not the same as Z converting it thereto, X represents a halogen atom, M represents an alkali metal or alkaline earth metal atom and n is an integer from 2 to 6, except where indicated otherwise, and, optionally, hydrolysing the product.

13. Process for preparing a compound of the formula:

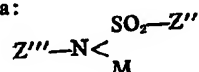


which comprises condensing a compound of the formula:



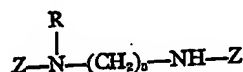
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with a compound of the formula:

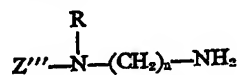


25 in which Z and R are as defined in claim 1 and n, M, Z'' , and Z''' , are as defined in claim 12, and hydrolysing the resulting product to remove the sulphonamide group

14. Process for preparing a compound of the formula:



which comprises condensing a compound of the formula:



with a compound of the formula:

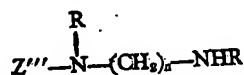


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in which Z, R and n are as defined in claim 1 and Z''' and Q_1 are as defined in claim 12 and, optionally, reacting the resulting compound with an amine.

30

15. Process for preparing a compound of formula II as defined in claim 2 which comprises condensing a compound of the formula:

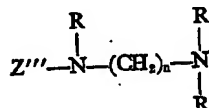


with a compound of the formula:

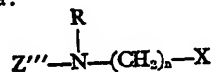


in which n and R are as defined in claim 1, and X and Z''' are as defined in claim 12.

16. Process for preparing a compound of formula III as defined in claim 3 which comprises condensing, with quaternisation, a compound of the formula:



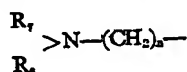
with a compound of the formula:



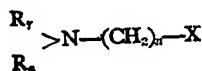
in which R is as defined in claim 1, n is as defined in claim 2, X is as defined in claim 3 and Z''' is as defined in claim 12.

17. Process for preparing a compound of formula I, II, or III as defined in claim 12 in which at least one of the R radicals represents a hydroxyalkyl radical which comprises reacting a compound of formula I, II, or III in which Z, E, m and R are as defined in claim 12 and in which at least one of the R radicals represents a hydrogen atom with a hydroxyalkyl halide:

18. Process for preparing a compound of formula I, II or III as defined in claim 12 in which at least one of the R radicals represents a radical of the formula:

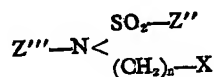


which comprises reacting a compound of formula I, II or III in which Z, E, m and R are as defined in claim 12 and in which at least one of the R radicals represents a hydrogen atom with a halogenoalkylamine of formula:

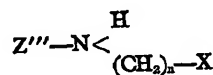


in which R₇, R₈ and n are as defined in claim 1 and X represents a halogen atom.

19. Process for preparing a compound of formula I, as defined in claim 12 which comprises condensing a compound of the formula:

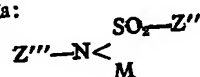


or of the formula:



42

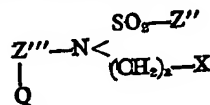
with a compound of the formula:



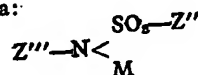
in which Z and n are as defined in claim 1 and Z'', Z''', X and M are as defined in claim 12, and hydrolysing the resulting product so as to remove the sulphonamide group or groups.

5

20. Process for preparing a compound of formula I, as defined in claim 12 which comprises condensing a compound of the formula:



with a compound of the formula:



10

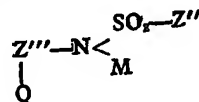
in which formulae n is as defined in claim 1, Z'', Z''', X and M are as defined in claim 12 and Q represents a halogen atom, reacting the resulting product with an amine of the formula:



15

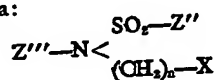
in which R_s is as defined in claim 12, and then hydrolysing to remove the sulphonamide groups.

21. Process for preparing a compound of formula I as defined in claim 12 which comprises condensing a compound of the formula:

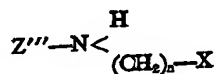


20

with a compound of the formula:



or of the formula:



25

in which n is as defined in claim 1, Z'', Z''', M and X are as defined in claim 12 and Q represents a halogen atom, reacting the resulting product with an amine of the formula:



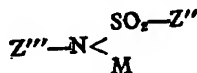
in which R_s is as defined in claim 12, and then hydrolysing to remove the sulphonamide groups.

30

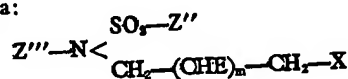
22. Process for preparing quaternary ammonium salts of compounds of formula I or II as defined in claim 12 which comprises reacting a tertiary amino group present in a compound of formula I or II in which Z, E, m and R is as defined in claim 12, with an alkyl (of 1 to 4 carbon atoms) halide, an aryl halide or an alkyl (of 1 to 4 carbon atoms) sulphate.

35

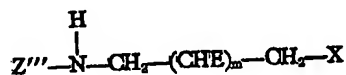
23. Process for preparing a compound of formula I as defined in claim 12 which comprises condensing a compound of the formula:



with a compound of the formula:

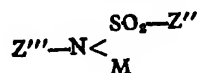


or of the formula:

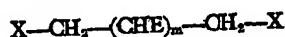


5 in which E and m are as defined in claim 1 and Z'', Z''', M and X are as defined in claim 12, and hydrolysing the product to remove the sulphonamide group or groups.

24. Process for preparing a compound of formula I as defined in claim 12 which comprises condensing a compound of the formula:



10 with a dihalogenoalkane of the formula:

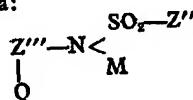


in which E and m are as defined in claim 1, and M, Z'', Z''' and X are as defined in claim 12 in the presence of dimethylformamide, and hydrolysing the sulphonamide groups.

15 25. Process for preparing a compound of formula I as defined in claim 12 which comprises condensing a dihalogenoalkane of the formula:



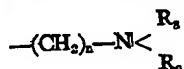
with a compound of the formula:



20 in which m and E are as defined in claim 1, X, M, Z'' and Z''' are as defined in claim 12 and Q represents a halogen atom such as chlorine or bromine, condensing the product with an amine of the formula:



25 in which R₅ represents an alkyl group of 1 to 4 carbon atoms, a hydroxyalkyl group of 1 to 4 carbon atoms, an alkoxyalkyl group or a radical of the formula:



in which R₆ and R₆ are as defined in claim 12, and hydrolysing the sulphonamide groups.

30 26. Process according to any one of claims 13 to 19 and 22 substantially as described in any one of Examples I to XI.

27. Process according to any one of claims 14 and 17 to 22 substantially as described in any one of Examples XII to XIX.

28. Process according to any one of claims 17, 18 and 23 to 25 substantially as described in any one of Examples XX to XXVIII.

35 29. A compound of formula I, II or III as defined in claim 12 whenever prepared by the process claimed in any one of claims 13 to 18 and 26.

30. A compound of formula I, II or III as defined in claim 12 whenever prepared by the process claimed in any one of claims 19 to 22 and 27.

40 31. A compound of formula I, II or III as defined in claim 12 whenever prepared by the process claimed in any one of claims 23 to 25 and 28.

32. A compound of formula I, II or III as defined in claim 12 whenever prepared by the process claimed in claim 12.

33. A composition suitable for dyeing keratinic fibres, especially human hair, which comprises at least one compound as claimed in any one of claims 1 to 11 and 29 to 32, in aqueous solution.

34. A composition according to claim 33 wherein the compound is present in an amount from 0.1% to 3% by weight.

35. A composition according to claim 33 or 34 which also contains a water-soluble dyestuff other than one claimed in any one of claims 1 to 11 and 29 to 32.

36. A composition according to claim 35 wherein the water-soluble dyestuff is a nitro, azo, or anthraquinone dyestuff.

37. A composition according to any one of claims 33 to 36 having a pH from 4 to 10.

38. A composition according to claim 37 having a pH from 6 to 9.

39. A composition according to any one of claims 33 to 38 which also contains an ingredient conventionally used in hair dye compositions.

40. A composition according to claim 39 which also contains a perfume, thickener or surface-active agent.

41. A composition according to any one of claims 33 to 40 wherein the compound is one claimed in any one of claims 6, 7, 9 and 29.

42. A composition according to any one of claims 33 to 40 wherein the compound is one claimed in either of claims 10 or 30.

43. A composition according to any one of claims 33 to 40 wherein the compound is one claimed in any one of claims 8, 11 and 31.

44. A composition according to claim 33 substantially as described in any one of Examples XXIX to XXXIII.

45. A composition according to claim 33 substantially as described in any one of Examples XXXIV to XXXIX and XLV.

46. A composition according to claim 33 substantially as described in any one of Examples XL and XLII to XLIV.

47. A composition according to claim 33 substantially as described in Example XLI.

48. A method of dyeing hair which comprises applying thereto a composition as claimed in any one of claims 33 to 47 for 5 to 30 minutes at a temperature of 15° to 35°C, and then rinsing and drying the hair.

49. A method according to claim 48 wherein the hair is bleached human hair.

50. A method according to claim 48 or 49 wherein the composition is one claimed in claim 41 or 44.

51. A method according to claim 48 or 49 wherein the composition is one claimed in claim 42 or 45.

52. A method according to claim 48 or 49 wherein the composition is one claimed in claim 43 or 46.

53. A method according to claim 48 substantially as described in Example XLI.

54. A method according to claim 50 substantially as described in any one of Examples XXIX to XXXIII.

55. A method according to claim 51 substantially as described in any one of Examples XXXIV to XXXIX and XLV.

56. A method according to claim 52 substantially as described in any one of Examples XL and XLII to XLIV.

J. A. KEMP & CO.,
Chartered Patent Agents,
14, South Square,
Gray's Inn, London, W.C.1.

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